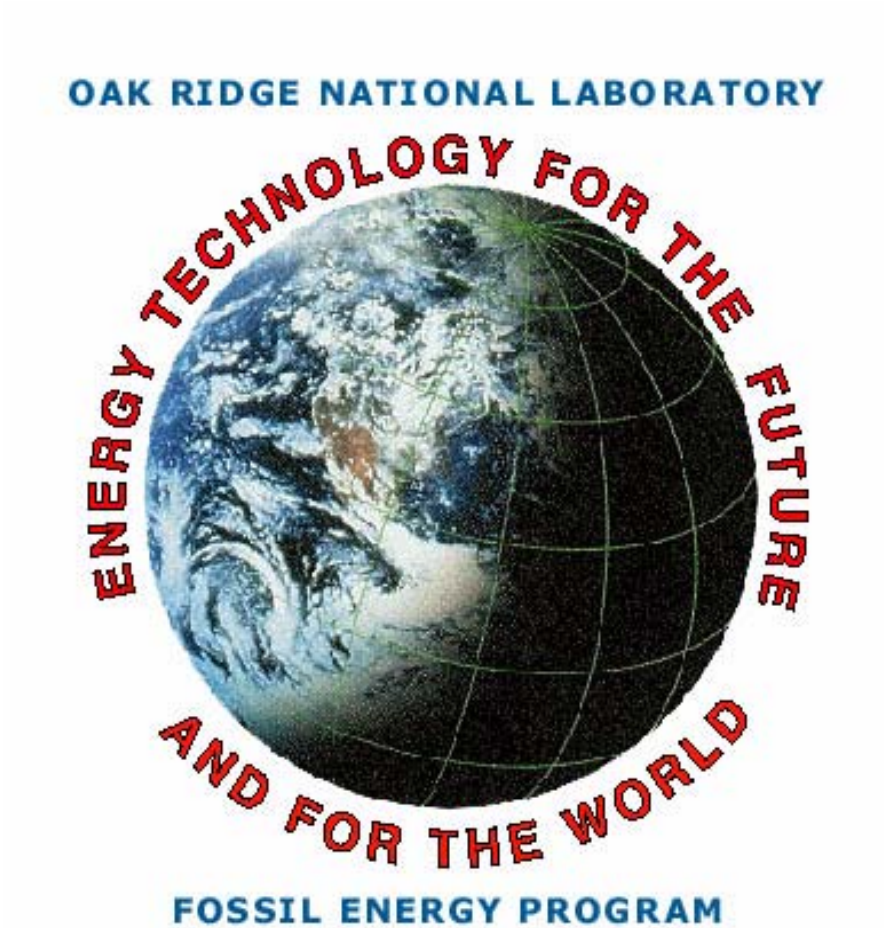
U. S. Department of Energy

Office of Fossil Energy

# ADVANCED RESEARCH MATERIALS PROGRAM



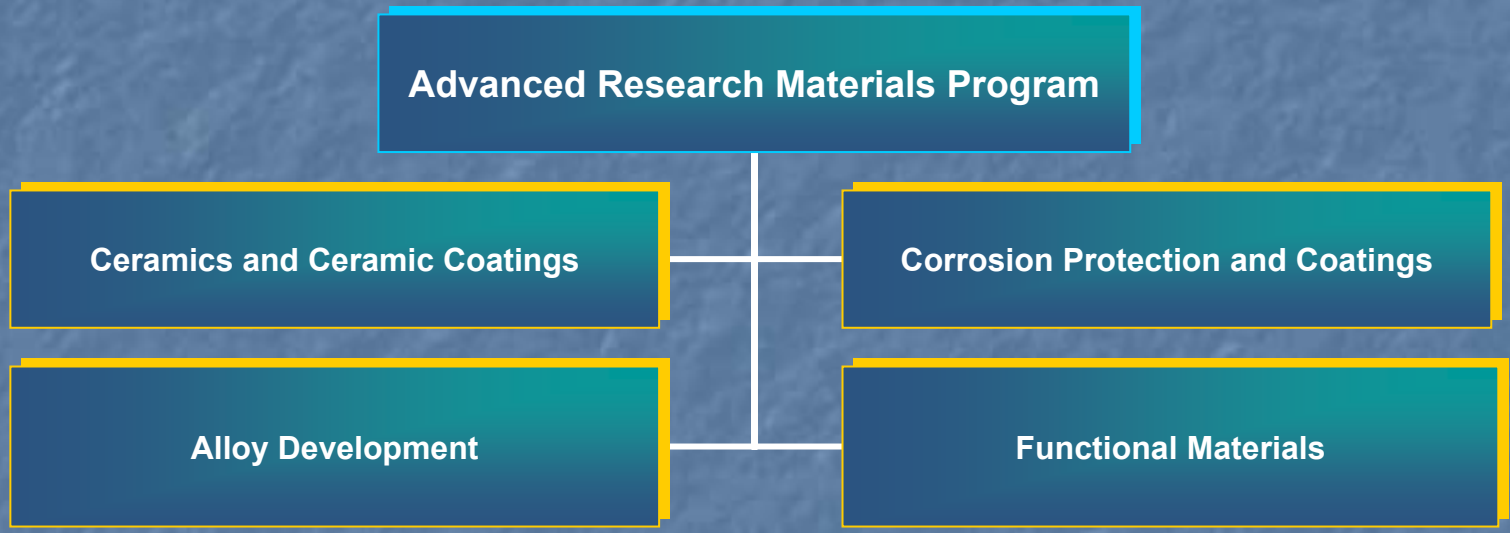

# MANAGEMENT REPORT FOR JULY - SEPTEMBER 2003

PAUL T. CARLSON

27 OCTOBER 2003

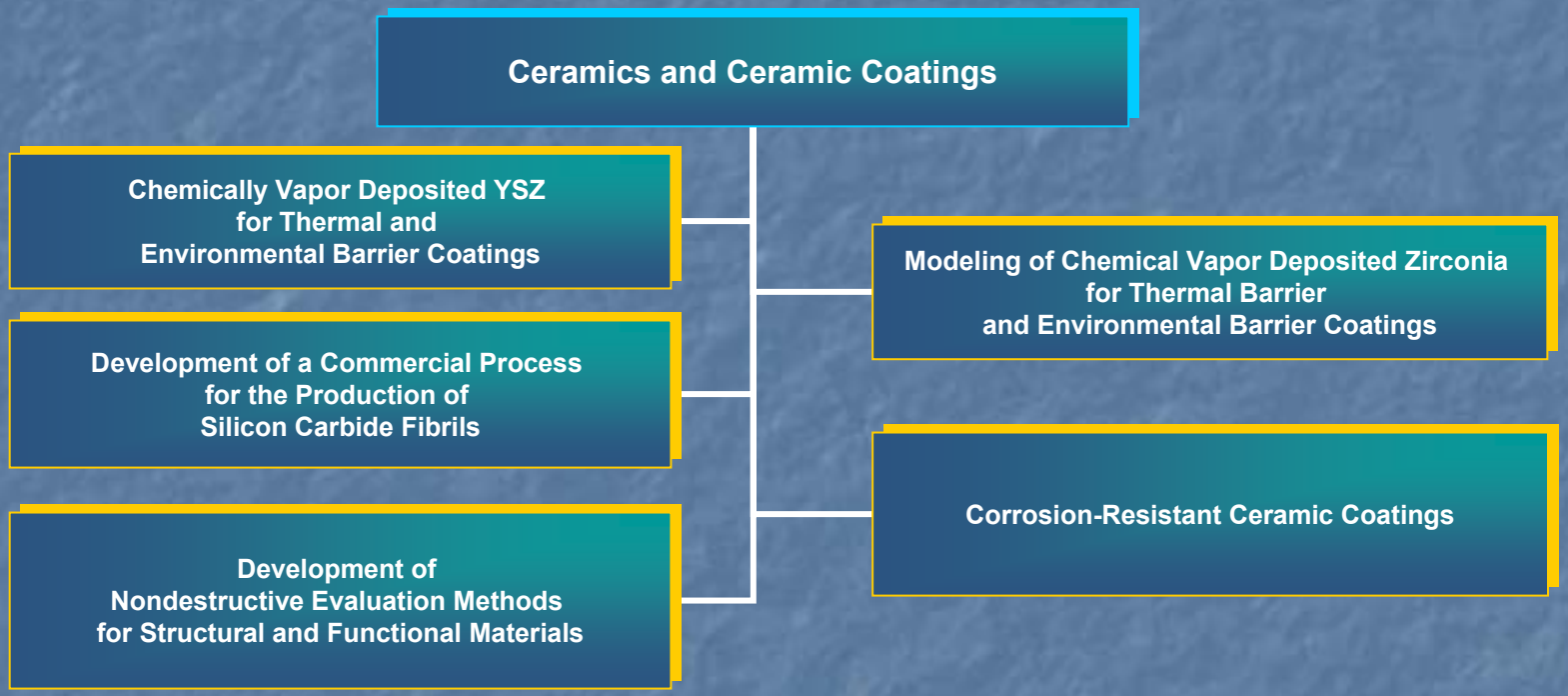
www.ornl.gov/fossil/

# Advanced Research Materials Program



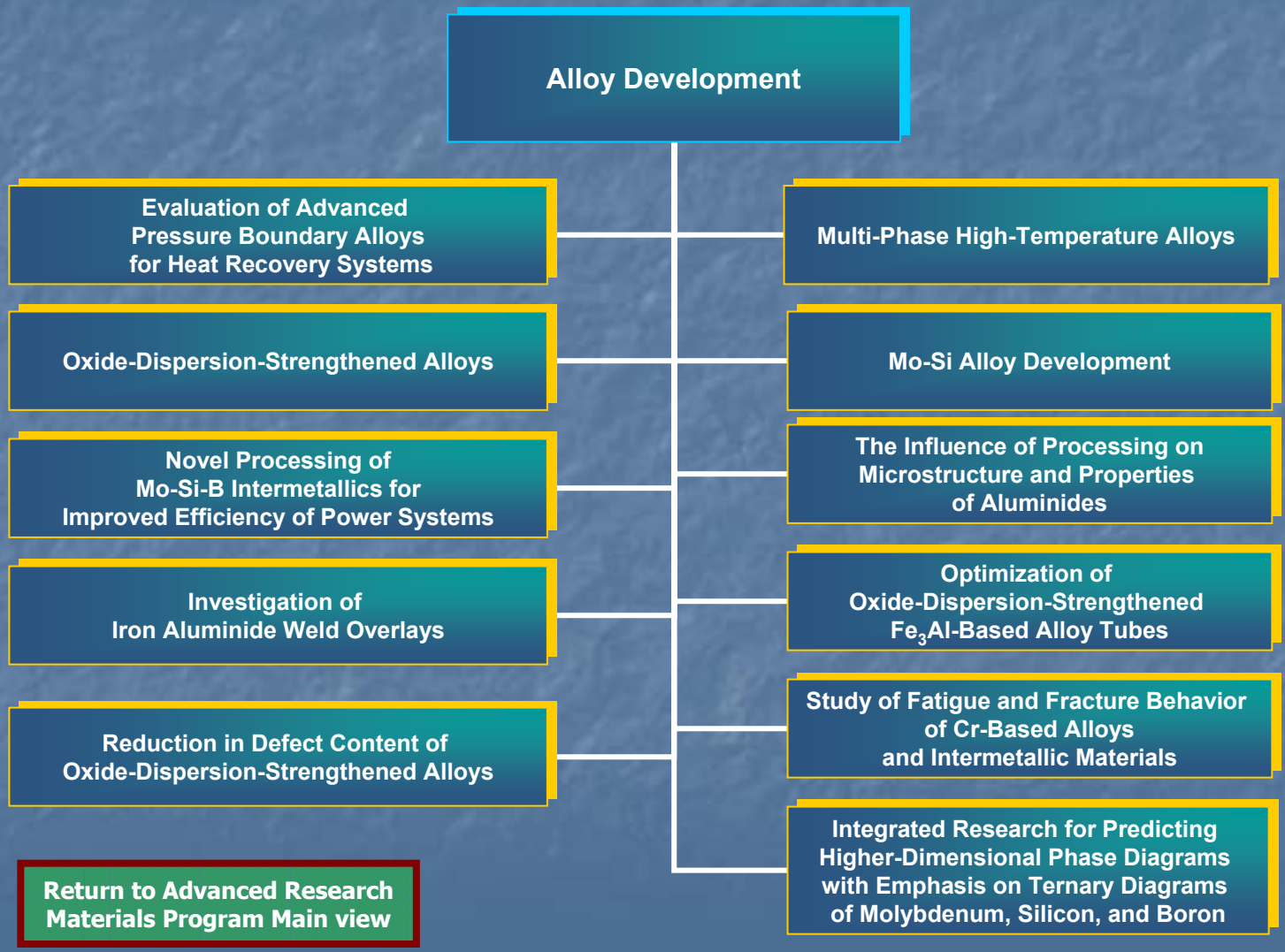

Click on Program area boxes to expand

# Ceramics and Ceramic Coatings

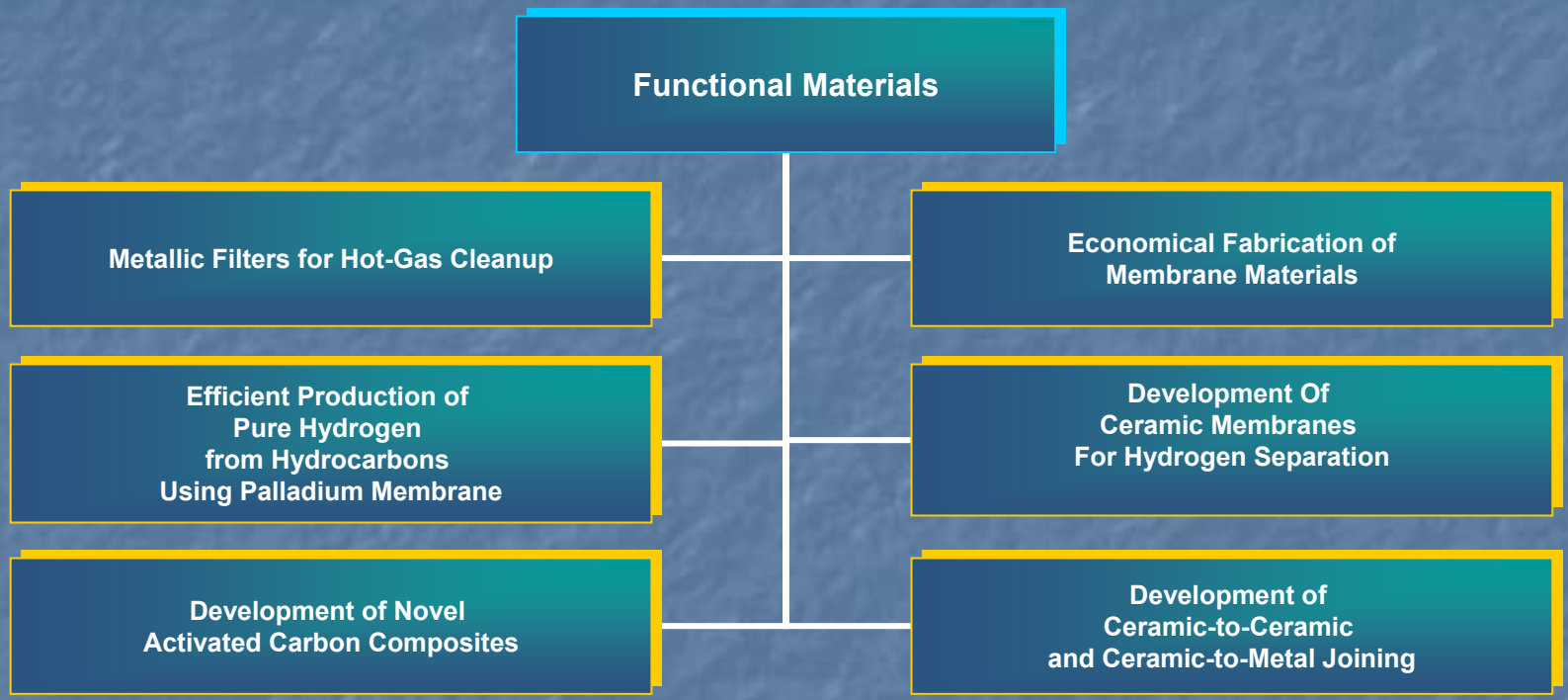



Return to Advanced Research Materials Program Main view

# Alloy Development

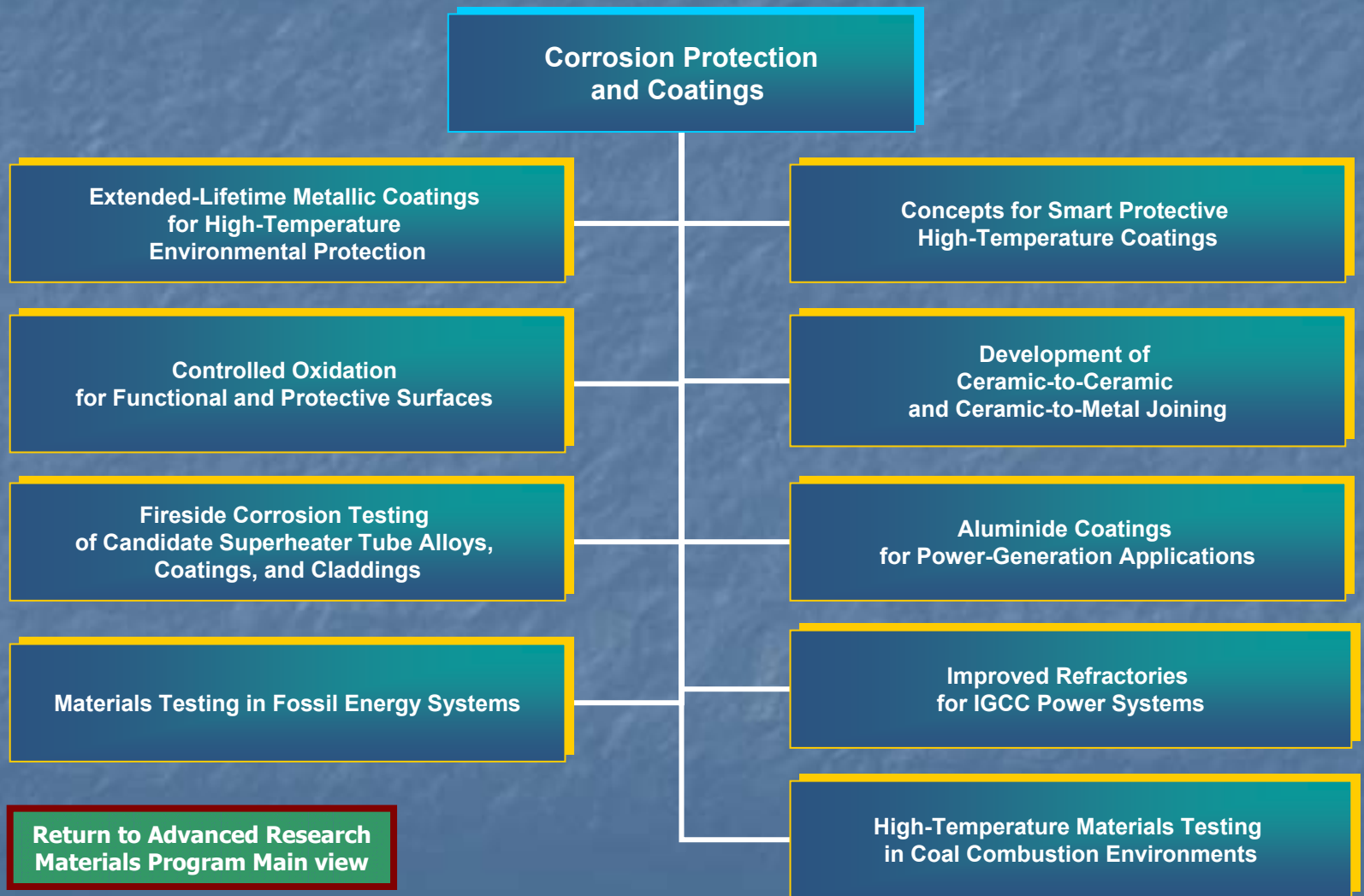


# Functional Materials




Return to Advanced Research Materials Program Main view

# Corrosion Protection and Coatings




Return to Advanced Research Materials Program Main view

# ADVANCED RESEARCH MATERIALS PROGRAM

**October 27, 2003**

| Organization | Project Title | Principal Investigator |
|---|---|---|
| Albany Research Center<br>1450 Queen Ave., SW<br>Albany, OR 97321 | Improved Refractories of IGCC Power Systems<br>ARC-4 | Cindy Dogan<br>(541) 967-5803<br>(541) 967-5845 (fax)<br>**dogan@alrc.doe.gov** |
| Ames Laboratory<br>Iowa State University<br>37 Wilhelm Hall<br>Ames, IA 50011 | Novel Processing of Mo-Si-B Intermetallics for Improved Efficiency of Power Systems<br>AMES-2 | Matt Kramer<br>(515) 294-0276<br>(515) 294-4291 (fax)<br>**mjkramer@ameslab.gov** |
| Ames Laboratory<br>126 Metals Development<br>Ames, IA 50011-3020 | Metallic Filters for Hot-Gas Cleanup<br>AMES-3 | Iver Anderson<br>(515) 294-9791<br>**andersoni@ameslab.gov** |
| Argonne National Laboratory<br>9700 South Cass Avenue<br>Argonne, IL 60439 | Development of Nondestructive Evaluation Methods for Structural and Functional Materials<br>ANL-1 | Bill Ellingson<br>(630) 252-5068<br>(630) 252-4798 (fax)<br>**ellingson@anl.gov** |
| | Fireside Corrosion of Materials for Advanced Combustion Systems<br>ANL-4 | Ken Natesan<br>(630) 252-5103<br>(630) 252-3604 (fax)<br>**natesan@anl.gov** |
| Foster Wheeler Development Corporation<br>John Blizard Research Center<br>12 Peach Tree Hill Road<br>Livingston, NJ 07039 | Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings<br>XSM401<br>FW-4 | Greg Stanko<br>Greg_Stanko@fw.com |
| Idaho National Engineering and Environmental Laboratory<br>P.O. Box 1625<br>MS 2025<br>Idaho Falls, ID 83415-2218 | The Influence of Processing on Microstructure and Properties of Aluminides<br>INEEL-2 | Richard Wright<br>(208) 526-6127<br>(208) 526-0690 (fax)<br>**rnw2@inel.gov** |
| Lehigh University<br>Whitaker Laboratory<br>5 East Packer Avenue<br>Bethlehem, PA 18015-3181 | Investigation of Iron Aluminide Weld Overlays<br>XSU604<br>LU-2 | Arnold Marder<br>(610) 758-4197<br>(610) 758-6407 (fax)<br>**Arm0@lehigh.edu** |

| Organization | Project Title | Principal Investigator |
|---|---|---|
| Los Alamos National Laboratory<br>Los Alamos, NM 87545 | Efficient Production of Pure Hydrogen from Hydrocarbons Using Palladium Membrane<br>LANL-3 | Steve Birdsell<br>1-505-667-5868<br>**birdsell@lanl.gov** |
| Oak Ridge National Laboratory<br>1 Bethel Valley Road<br>P. O. Box 2008<br>Oak Ridge, TN 37831 | *Materials and Components in Fossil Energy Applications* Newsletter<br>MCNL-5 | Ian Wright<br>(865) 574-4451<br>**wrightig@ornl.gov** |
| | Chemically Vapor Deposited YSZ for Thermal and Environmental Barrier Coatings<br>ORNL-1(A) | Ted Besmann<br>(865) 574-6852<br>**besmanntm@ornl.gov** |
| | Corrosion-Resistant Ceramic Coatings<br>ORNL-1(B) | Beth Armstrong<br>(865) 241-5862<br>**armstrongbl@ornl.gov** |
| | Extended-Lifetime Metallic Coatings for High-Temperature Environmental Protection<br>ORNL-2(B) | Bruce Pint<br>(865) 576-2897<br>**pintba@ornl.gov** |
| | Evaluation of Advanced Pressure Boundary Alloys for Heat Recovery Systems<br>ORNL-2(C) | Bob Swindeman<br>(865) 574-5108<br>**swindemanrw@ornl.gov** |
| | Multi-Phase High-Temperature Alloys<br>ORNL-2(D) | Mike Brady<br>(865) 574-5153<br>**bradymp@ornl.gov** |
| | Oxide-Dispersion-Strengthened Alloys<br>ORNL-2(E) | Ian Wright<br>(865) 574-4451<br>**wrightig@ornl.gov** |
| | Mo-Si Alloy Development<br>ORNL-2(I) | Joachim Schneibel<br>(865) 574-4644<br>**schneibeljh@ornl.gov** |
| | Inorganic Membrane Development<br>ORNL-3(B) | Rod Judkins<br>(865) 574-4572<br>judkinsrr@ornl.gov |

| Organization | Project Title | Principal Investigator |
|---|---|---|
| | Development of Novel Activated Carbon Composites<br>ORNL-3(E) | Tim Burchell<br>(865) 576-8595<br>**burchelltd@ornl.gov** |
| | Economical Fabrication of Membrane Materials<br>ORNL-3(H) | Tim Armstrong<br>(865) 574-7996<br>**armstrongt@ornl.gov** |
| | Controlled Oxidation for Functional and Protective Surfaces<br>ORNL-4(A) | Peter Tortorelli<br>(865) 574-5119<br>**tortorellipf@ornl.gov** |
| | Concepts for Smart Protective High-Temperature Coatings<br>ORNL-4(C) | Peter Tortorelli<br>(865) 574-5119<br>**tortorellipf@ornl.gov** |
| | Management of the Fossil Energy Advanced Research Materials Program<br>ORNL-5(A) | Rod Judkins<br>(865) 574-4572<br>judkinsrr@ornl.gov |
| Pacific Northwest National Laboratory<br>PSL-3000 Area<br>Richland, WA 99352 | Development of Ceramic-to-Ceramic and Ceramic-to Metal Joining<br>PNNL-3 | Scott Weil<br>(509) 375-6796<br>(509) 375-2186 (fax)<br>**scott.weil@pnl.gov** |
| ReMaxCo Technologies, Inc.<br>1010 Commerce Park Drive<br>Suite I<br>Oak Ridge, TN 37830 | Development of a Commercial Process for the Production of Silicon Carbide Fibrils<br>XSZ337<br>REMAXCO-5 | Dick Nixdorf<br>(865) 483-5060<br>(865) 482-3938 (fax)<br>**nixdorfr@indceramicsolns.com** |
| Tennessee Technological University<br>Center for Manufacturing Research<br>College of Engineering<br>Campus Box 5077<br>Cookeville, TN 38505 | Aluminide Coatings for Power-Generation Applications<br>4000007035<br>TTU-2 | Ying Zhang<br>(931) 372-3186<br>(931) 372-6340 (fax)<br>**Yzhang@tntech.edu**<br>zhangy@ornl.gov |
| University of California at San Diego<br>Department of Applied Mechanics and Engineering Sciences<br>La Jolla, CA 92093-0411 | Optimization of Oxide-Dispersion-Strengthened $Fe_3Al$-Based Alloy Tubes<br>XSY009<br>UCSD-2 | Bimal Kad<br>(619) 534-7059<br>(619) 534-7466 (fax)<br>**bkad@ucsd.edu** |

| Organization | Project Title | Principal Investigator |
|---|---|---|
| The University of Liverpool<br>Liverpool, United Kingdom<br>L69 3BX | Reduction in Defect Content of ODS Alloys<br>XSY382<br>UL-2 | Andy Jones<br>151-794-8026<br>a.r.jones@liv.ac.uk |
| University of Louisville<br>Dept of Chemical Engineering<br>Speed Scientific School<br>Louisville, KY 40292 | Modeling of Chemical Vapor Deposited Zirconia for Thermal Barrier and Environmental Barrier Coatings<br>4000016368<br>UOL-1 | Tom Starr<br>(502) 852-1073<br>(502) 852-6355(fax)<br>tom.starr@louisville.edu |
| University of North Dakota<br>Energy and Environmental Research Center<br>15 North 23rd Street<br>Grand Forks, ND 56202 | Materials Testing in Fossil Energy Systems<br>XSS112<br>UNDEERC-4 | John Hurley<br>(701) 777-5159<br>(701) 777-5181 (fax)<br>jhurley@undeerc.org |
| University of Tennessee<br>Dept of Materials Science and Engineering<br>Knoxville, TN 37996-2200 | Study of Fatigue and Fracture Behavior of Cr-Based Alloys and Intermetallic Materials<br>XSP173<br>UT-2(A) | Peter Liaw<br>(865) 974-6356<br>(865) 974-4115 (fax)<br>liaw@utkux1.utk.edu |
| West Virginia University<br>Department of Physics<br>Morgantown, WV 26506-6315 | Integrated Research for Predicting Higher-Dimensional Phase Diagrams with Emphasis on Ternary Diagrams of Molybdenum, Silicon, and Boron<br>40000013127<br>WVU-2 | Bruce Kang<br>304 293-3111 x2316<br>kang@cemr.wvu.edu |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| MCNL-5 | US Department of Energy-EPRI Newsletter on Materials and Components in Fossil Energy Applications | FEAA028 | | |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| ORNL | I. G. Wright |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 2 |
| **Total Current Year Commitment $K]** | 58 |
| **Projected Current Year Costs [$K]** | 58 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 58 |
| **Actual Costs** | 3 | 12 | 12 | 15 | 20 | 22 | 25 | 26 | 28 | 30 | 34 | 36 |
| **Variance** | 2 | (2) | 3 | 5 | 5 | 8 | 10 | 14 | 17 | 20 | 21 | 22 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| MCNL-5-40 | Publish Issue No. 158 | 06/01/02 | 10/28/02 | 10/28/02 |
| MCNL-5-41 | Publish Issue No. 159 | 08/01/02 | 11/15/02 | 01/02/03 |
| MCNL-5-42 | Publish Issue No. 160 | 10/01/02 | 01/31/03 | 09/25/03 |
| MCNL-5-43 | Publish Issue No. 161 | 01/01/04 | | |
| MCNL-5-44 | Publish Issue No. 162 | 04/01/04 | | |
| MCNL-5-45 | Publish Issue No. 163 | 07/01/04 | | |
| MCNL-5-46 | Publish Issue No. 164 | 10/01/04 | | |
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## TECHNICAL HIGHLIGHTS

Preparation of issue No. 160 was completed, with the following articles:

- Premature Failure of T-91 Superheater Tubes in an HRSG
- Oxide Exfoliation from Alloy 347HFG in a
- High-Temperature Steam Boiler
- Fate of Trace Contaminants from Biomass Fuels in Gasification Systems
- Feasibility Studies for On-Line Electrochemical Corrosion Monitoring in Fireside Applications
- Separation of CO2 from Coal-Based Power Plants
- Meetings Calendar
- Calls for Papers
- A Word From Our Sponsor

## ISSUES

In the wake of EPRI's withdrawal of support for the Newsletter, some changes have been made in the procedures used to it with the intent of continuing publication at the rate of 4 issues per year. This is the first issue under the new regime.

| Report Prepared By | Date |
|---|---|
| I. G. Wright | 10/15/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-5(A) | Management of the Advanced Research Materials Program | FEAA028 | 10/01/79 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>P. O. Box 2008<br>Oak Ridge, TN 37831 | R. R. Judkins<br>P. T. Carlson<br>I. G. Wright |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 211 |
| **Total Current Year Commitment $K]** | 400 |
| **Projected Current Year Costs [$K]** | 500 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 42 | 85 | 127 | 169 | 212 | 254 | 296 | 339 | 381 | 423 | 466 | 500 |
| **Actual Costs** | 22 | 45 | 69 | 92 | 124 | 161 | 195 | 225 | 257 | 300 | 330 | 365 |
| **Variance** | 20 | 40 | 58 | 77 | 88 | 93 | 101 | 114 | 124 | 123 | 136 | 135 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ORNL-5(A)-1 | Complete review of revised FWPs for FYs 2002-2004 from other national laboratories, and provide comments by letter to DOE and national laboratories. | 10/31/02 | | 09/10/02 |
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## TECHNICAL HIGHLIGHTS

No items of significance to report.

## ISSUES

None.

| Report Prepared By | Date |
|---|---|
| Paul T. Carlson | 10/07/03 |

# Quarterly Management Report

FY 2003

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| LU-2 | Effect of Chromium on Fe/Al Weld Overlay Coatings for Corrosion Protection... | 19X-SU604V | 12/15/95 | 06/27/04 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Lehigh University<br>Office of Research and Sponsored Programs<br>526 Brodhead Avenue<br>Bethlehem, PA 18015 | Dr. John N. DuPont<br>Dr. Arnold R. Marder<br>Jonathan Regina |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 245 |
| **Total Current Year Commitment $K]** | 116 |
| **Projected Current Year Costs [$K]** | 90 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 5 | 5 | 5 | 8 | 5 | 5 | 5 | 5 | 13 | 13 | 13 | 8 |
| **Actual Costs** | 0 | 2 | 0 | 1 | 2 | 8 | 3 | 7 | 5 | 15 | 2 | 5 |
| **Variance** | 5 | 3 | 5 | 7 | 3 | (3) | 2 | (2) | 8 | (2) | 11 | 3 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| Task 1 | Weldability Study of Fe-Al-Cr Alloys | 07/15/03 | | |
| Task 2 | Gaseous and Solid State Laboratory Corrosion Studies | 03/15/04 | | |
| Task 3 | Characterization of Fe-Al-Cr Welds (TEM) - beginning August, 2003 | 01/31/04 | | |
| Task 4 | Final Report Preparation - beginning June, 2004 | 06/15/04 | | |
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## TECHNICAL HIGHLIGHTS

Since the last report, the FeAlCr weld overlay weldability portion of the study (Task 1) has been completed. Welds were deposited using pure aluminum filler metal wire and 430 stainless steel filler metal wire onto a plain carbon steel substrate (A285). The filler metal feed speeds ranged from 35ipm (15mm/s) to 175ipm (74mm/s) to obtain welds with a wide range of aluminum and chromium concentrations. The welding current and travel speed were kept constant at 225amps and 2mm/s, respectively. Characterization of the FeAlCr weld overlays were conducted using Electron Probe Microanalysis (EPMA), which was used to obtain quantitative compositional linescans through various areas of select welds. These linescans were used to determine if the welds were homogeneous and if any microsegregation occurred within the welds. EPMA linescans were first taken of weld overlay cross-sections across the width of the weld and from the top of the weld into the base metal. These linescans performed on select samples (Fe-7.5wt%Al, Fe-8%Al-2.5%Cr, Fe-9.5%Al-8.5%Cr, and Fe-9%Al-12%Cr) showed that no macrosegregation of alloying elements (Fe, Al, and Cr) occurred throughout the weld cross-section. The compositional linescans performed from the crown of the weld into the base metal showed that the largest partially mixed zone (PMZ) present in the analyzed weld overlays was only 0.5mm wide.

Then, longitudinal linescans were taken on samples that were extracted from the weld overlay along the direction of the weld. These linescans showed that welds did not deviate in composition through the length of the weld overlay. The combination of these linescan results indicated that no macrosegregation occurred within the weld overlays and they were considered to be macroscopically homogeneous. Compositional linescans were also taken across entire weld grains on select weld overlays (Fe-14.5%Al, Fe-10%Al-5%Cr, and Fe-6%Al-13%Cr) to determine if any microsegregation occurred within the welds. The results from these linescans showed that neither aluminum nor chromium segregated within the weld grains and the welds were therefore also considered to be microscopically homogeneous.

Bulk weld compositions were also obtained by using EPMA with a large scan area. The bulk compositional results showed that at lower aluminum concentrations (6-9wt%Al), chromium additions up to approximately 11-12%Cr could be incorporated into the weld overlays before cracking occurred above approximately 12%Cr. Crack free welds were able to be deposited at higher aluminum concentrations (9-12.5wt%Al) up to approximately 4-5%Cr, where cracking occurred above 5%Cr. Binary Fe-Al weld overlays were found to be crack-free up to approximately 15wt%Al, and sensitive to hydrogen cracking above this binary concentration. Now that the weldability study is complete, characterization of the phases present within the weld overlays will be determined in order to understand the mechanism behind the susceptibility to hydrogen cracking. Several weld overlay compositions will also be selected for corrosion testing. Cast alloys of equivalent composition will be made and used for long term corrosion testing.

## ISSUES

None.

| Report Prepared By | Date |
|---|---|
| Dr. John N. DuPont and Jonathan Regina | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-1(A) | Chemically Vapor Deposited YSZ for Thermal and Environmental Barrier Coatings | FEAA028 | 10/01/82 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>P. O. Box 2008<br>Oak Ridge, TN 37831-6063 | T. M. Besmann |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | |
| Total Current Year Commitment $K] | |
| Projected Current Year Costs [$K] | |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 6 | 26 | 61 | 76 | 92 | 107 | 123 | 138 | 153 | 169 | 184 | 209 |
| Actual Costs | 3 | 16 | 27 | 36 | 53 | 78 | 105 | 125 | 140 | 162 | 185 | 210 |
| Variance | 3 | 10 | 34 | 40 | 39 | 29 | 18 | 13 | 13 | 7 | (1) | (1) |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ORNL-1(A) 1 | An open literature publication on the kinetics and modeling of YSZ deposition will be submitted for publication. | 03/02/02 | 12/31/02 | 11/30/02 |
| ORNL-1(A) 2 | An extensive set of deposition rate date will be developed that will provide a basis for development of a kinetic model for YSZ deposition. | 09/02/02 | | 09/02/02 |
| ORNL-1(A) 3 | An open literature publication on the use of CVD YSZ on turbine blades will be submitted for publication. | 03/31/03 | 05/31/03 | 05/31/03 |
| ORNL-1(A) 4 | Sets of nickel-superalloy samples with appropriate bond coats will be coated with YSZ and subject to evaluation. | 09/30/03 | 05/31/04 | |
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## TECHNICAL HIGHLIGHTS

Using yttrium and zirconium n-butoxide precursors (dissolved in butanol and toluene solvents, respectively) and molecular oxygen, YSZ was fabricated at an estimated (by weight gain) 42 mm hr-1 (~1200oC). Temperature studies showed the YSZ growth rate had strong temperature dependence below 1100oC with activation energy of 65.03 + 0.212 kJ mol-1. X-ray diffraction showed tetragonal YSZ formation on Mar-M247 super-alloy blades. Columnar microstructures were observed under SEM. Thicknesses were measured using SEM and the software package PAX-IT. The maximum measured deposition rate was 43 mm hr-1 (at 1200oC), which agreed well with the estimated data above.

## ISSUES

| Report Prepared By | Date |
| --- | --- |
| | |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-1(B) | Corrosion Resistant Coatings | FEAA028 | 10/01/99 | 09/30/31 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>P.O. Box 2008<br>Oak Ridge, TN 37831-6063 | B.L. Armstrong |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 115 |
| Total Current Year Commitment $K] | 250 |
| Projected Current Year Costs [$K] | 365 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 | 270 | 300 | 330 | 365 |
| Actual Costs | 38 | 60 | 65 | 79 | 99 | 126 | 159 | 172 | 187 | 213 | 243 | 295 |
| Variance | (8) | 0 | 25 | 41 | 51 | 54 | 51 | 68 | 83 | 87 | 87 | 70 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ORNL-1(B)-1 | Complete the deposition and evaluation of the second series conversion coatings designed to produce scales other than silica | 03/30/03 | | 03/30/03 |
| ORNL-1(B)-2 | Complete evaluation of materials tested fY2001 NETL CERF run. | 09/30/03 | 03/30/04 | |
| ORNL-1(B)-3 | Evaluate dip coating processing conditions for mullite as a function of coating density, coating thickness, coating adherence, and corrosion resistance. | 09/30/03 | 03/30/04 | |
| ORNL-1(B)-4 | Evaluate dip coating processing condition for a silicate based material other than mullite as a function of coating density, coating thickness, coating adherence, | 09/30/04 | | |
| ORNL-1(B)-5 | Complete the deposition and evaluation of a new solution based conversion coatings designed to produce scales other than silica. | 09/30/05 | | |
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## TECHNICAL HIGHLIGHTS

Review: In order to utilize the attractive properties of SiC, additional measures must be employed to protect the material from corrosive environments. In many cases, systems are being developed that combine oxide and non-oxide ceramics to take advantage of the properties of both families of materials. For example, oxide ceramic coatings are being deposited on SiC and silicon nitride ceramics to protect the bulk materials from corrosion. Unfortunately, the oxide coatings do not completely prevent oxygen diffusion and thus a silica layer is formed between the substrate and the coating. Due to a low modulus and coefficient of thermal expansion (CTE), silica is not compatible with either the coating or the substrate. It is believed that the silica layer will continue to grow with time, albeit very slowly, and eventually cause the coating to fail and spall during thermal cycling. This program has been investigating several approaches to improving the environmental stability of SiC and silicon based materials. One approach that is being taken is to coat the surface of a hexaloy SiC substrate using slurry based coatings.

Results: Development continues on the improvement of dip coat slurry stability through the evaluation of alternative dispersants and binder systems. Sedimentation, rheology, surface charge, and dipping (characterization of coating thickness and uniformity as a function of slurry and dip variables) experiments continue.

Evaluation of the activities and reactivity of candidate materials in controlled environments continues. Collaboration with Peter Tortorelli (ORNL) continues. Several candidate materials including mullite, doped alumino-silicates, rare earth or lanthanide series doped disilicates, and calcium aluminate have been fabricated and densified. Testing has begun on the calcium aluminates and the doped alumino-silicates in the microbalance/TGA. Ted Besmann and Nagraj Kulkarni will be assisting in the thermodynamic modeling of the solid-gas phase relationship in these test condiitons. In addition, the data that has been collected on this project and other collaborative projects will be collected and sorted into a database for future reference and publication.

Work continued on the investigation of new or alternative coating materials. Calcium aluminate was identified as a potential coating material system during some investigation previously this fiscal year. After the initial results from the microbalance, the fabrication of test bars for mechanical property evaluation before and after exposure to high temperature, thermal cycling, high temperature steam, and molten salt was initiated and has been completed. The high temperature thermal cycling runs have been completed, and the remaining test bars are awaiting furnace availability.

Analysis of the samples returned from the NETL/CERF run this past year continues. SEM analysis of the ceramic samples is on-going. Approximately 60 of the 80 samples have been analyzed to date.

## ISSUES

None to report.

| Report Prepared By | Date |
|---|---|
| B.L. Armstrong | 10/01/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-2(B) | Extended-Lifetime Metallic Coatings for High-Temperature Environmental Protection | FEAA028 | 10/01/02 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>P.O. Box 2008<br>Oak Ridge, Tennessee 37831 | B.A. Pint, P.F. Tortorelli, and I.G. Wright |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 12 |
| **Total Current Year Commitment $K]** | 20 |
| **Projected Current Year Costs [$K]** | 207 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 18 | 36 | 54 | 72 | 90 | 107 | 126 | 143 | 159 | 175 | 191 | 207 |
| **Actual Costs** | 15 | 32 | 55 | 69 | 82 | 100 | 124 | 139 | 154 | 195 | 203 | 210 |
| **Variance** | 3 | 4 | (1) | 3 | 8 | 7 | 2 | 4 | 5 | (20) | (12) | (3) |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ORNL-2(B)-1 | Complete study of composition on Fe-Al oxidation behavior. | 05/31/03 | | 05/31/03 |
| ORNL-2(B)-2 | Complete draft report on modeling work. | 09/30/03 | 12/31/03 | |
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## TECHNICAL HIGHLIGHTS

As part of the effort to optimize the compositions of iron-based alumina-forming coatings, the effect of the use of two or more reactive elements (RE's) to optimize oxidation performance of alloys is being evaluated. When done correctly, such co-doping was found to improve scale adhesion and slow scale growth rates compared to similar alloy compositions with single RE additions. The addition of two or more RE's did not appear to result in any significant change in the alumina scale microstructure or the amount of ionic segregation on its grain boundaries. Dopant optimization resulted in a >30% increase in the time to failure in 1h cycles at 1200°C of co-doped FeCrAl compared to FeCrAl+Y. The increased performance with reduced doping levels suggests that RE dopants are effective when located on the scale grain boundaries as ions, but when they form RE-rich oxides beneath or within the alumina scale they diminish the beneficial RE effect.

## ISSUES

None.

| Report Prepared By | Date |
|---|---|
| B. A. Pint | 10/06/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| TTU-2 | Aluminide Coatings for Power-Generation Applications | 4000007035 | 01/21/01 | 12/31/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Ying Zhang<br>Department of Mechanical Engineering<br>TTU Box 5014<br>115 W 10th Street<br>Tennessee Technological University, Cookeville, TN 38505-0001 | Ying Zhang |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 30 |
| **Total Current Year Commitment $K]** | 78 |
| **Projected Current Year Costs [$K]** | 85 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 4 | 21 | 30 | 33 | 34 | 35 | 38 | 48 | 59 | 70 | 77 | 85 |
| **Actual Costs** | 4 | 21 | 23 | 25 | 27 | 35 | 38 | 44 | 55 | 67 | 69 | 72 |
| **Variance** | 0 | 0 | 7 | 8 | 7 | 0 | 0 | 4 | 4 | 3 | 8 | 13 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| TTU-2-1 | Task I. Aluminide Coatings on Fe-based Alloys | 09/30/03 | | 08/31/03 |
| | To better understand the key issues for achieving long oxidation lifetimes with aluminide coatings on iron-based substrates | | | |
| | • CTE mismatch between the coating and substrate alloys<br>• Al backdiffusion (loss of Al to substrate) | | | |
| TTU-2-2 | Task II. Aluminide Coatings on Ni-based Superalloys | 09/30/03 | | 09/30/03 |
| | To investigate the effect of reactive elements (such as Hf) in superalloy substrates on the oxidation behavior of NiAl and (Ni,Pt)Al coatings | | | |
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## TECHNICAL HIGHLIGHTS

Task I – Aluminide Coatings on Fe-Base Alloys

• The diffusion tests are being conducted on the coated steel specimens in air for times up to 10,000h (~1.14yr) in the temperature range of 500-800°C.

One of the critical issues for the application of iron aluminide coatings is the loss of Al from the coating into the Fe-base substrate alloys which do not contain aluminum. The interdiffusion behavior between chemical vapor deposited (CVD) aluminide coatings and ferritic and austenitic substrates is being studied for times up to 10,000h in the temperature range of 500-800°C. Coatings were synthesized using a laboratory-scale CVD reactor on representative commercial ferritic (Fe-9Cr-1Mo) and austenitic (type 304L stainless steel) alloys. The aluminide coatings on both alloys typically consisted of a relatively thin (20-25μm) Al-rich outer layer and a thicker (150-250μm) inner layer with less Al. The composition profiles before and after interdiffusion testing were measured by electron probe microanalysis (EPMA). The decrease of the Al content at the coating surface was not significant after extended diffusion times (up to 5000h) at temperatures below700°C. More interdiffusion occurred at 800°C in coatings on both Fe-9Cr-1Mo and 304L alloys. Particularly, a two-phase microstructure was formed in the outer coating layer on 304L after interdiffusion of 2000h at 800°C. A computer model COSIM (Coating Oxidation and Substrate Interdiffusion Model), which was originally developed for MCrAlY overlay coatings by NASA, was applied to simulate the interdiffusion behavior of the iron aluminide coatings and to predict coating lifietime. Another mathematic model developed by Heckel in the 70's concerning the kinetics of phase layer growth during aluminization of iron and during subsequent diffusion heat treatment also was used to calculate the surface Al concentration and the coating thickness after the diffusion tests. A reasonable agreement was obtained between the simulated and experimental composition profiles for coatings on Fe-9Cr-1Mo. Simplification of the quaternary Fe-Ni-Cr-Al system of the coatings on 304L to either a binary or ternary system, as well as lack of diffusion data led to the discrepancy between calculated and measured composition profiles. This work is being summarized for a journal paper.

• Submitted a paper entitled "The Effect of Water Vapor on the Oxidation Behavior of CVD Iron Aluminide Coatings" (Y. Zhang, B. A. Pint, J. A. Haynes, and P. F. Tortorelli) to Oxidation of Metals

• Poster presentation entitled "Critical Issues in Aluminide Coatings for Power Generation Applications" (Y. Zhang, B. A. Pint, J. A. Haynes, K. M. Cooley, and I. G. Wright) at the Gordon Research Conference of High Temperature Corrosion, Colby-Sawyer College, New London, NH, July 20-23, 2003

Task II – Aluminide Coatings on Ni-Base Superalloys

• Platinum coatings with relatively good adherence and uniform thickness were obtained by a laboratory electroplating process

Based on the results from previous electroplating experiments, a plating current density of 0.20A/dm2 was identified as the appropriate current density for obtaining an adherent Pt layer with a relatively uniform thickness distribution and at a reasonable plating rate. Several René 142 superalloy coupons were plated by using the identified plating parameters. The electroplated Pt was uniform in thickness and demonstrated metallic shininess. No spallation was observed after Scotch tape test which indicated reasonably good adherence. Selected Pt-plated René 142 specimens also were aluminized by a low-activity CVD process. Some blisters were noticed on the surface of the CVD platinum aluminide coatings. SEM characterization suggests that these blisters exist near the coating surface area without deep penetration into the coating. A post-plating annealing treatment prior to the CVD aluminizing process is being considered to reduce residual stress and therefore further improve adherence of the electro-plated Pt layer.

• Completed cyclic oxidation testing on the CVD NiAl-coated René 142 superalloy specimens with various Hf contents

The directionally-solidified (DS) René 142 superalloy specimens with three Hf levels (0.02 wt.%, 0.76 wt.% and 1.37 wt.%) were aluminized in an ultra-clean laboratory CVD reactor. The NiAl coating thickness measured from the original substrate was ~25μm and the Al concentration was ~40 at.%. Cyclic oxidation testing was conducted at 1100°C and 1150°C. Spallation was observed in all NiAl coating specimens disregarding the Hf contents, which was not as expected. The milestone of the Task II was met for NiAl coatings but that the related work on (Ni,Pt)Al will not be pursued to devote more resources to higher priority issues associated with iron aluminide coatings.

## ISSUES

| Report Prepared By | Date |
|---|---|
| Ying Zhang | 09/15/03 |

# Quarterly Management Report

2003

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| UOL-1 | Modeling of CVD Zirconia for Thermal Barrier and Environmental Barrier Coatings | 4000016368 | 10/01/02 | 09/30/05 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Thomas L. Starr<br>Chemical Engineering Department<br>University of Louisville<br>Louisville,KY 40292 | Thomas L. Starr |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 0 |
| **Total Current Year Commitment $K]** | 84 |
| **Projected Current Year Costs [$K]** | 81 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 7 | 14 | 21 | 24 | 29 | 35 | 43 | 51 | 59 | 67 | 75 | 84 |
| **Actual Costs** | 5 | 11 | 18 | 24 | 29 | 35 | 40 | 46 | 54 | 64 | 73 | 81 |
| **Variance** | 2 | 3 | 3 | 0 | 0 | 0 | 3 | 5 | 5 | 3 | 2 | 3 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| UOL-1-1 | Identify method to increase YSZ deposition rate | 04/30/03 | | 03/31/03 |
| UOL-1-2 | Model deposition for vane/blade geometry | 09/30/03 | | 09/30/03 |
| UOL-1-3 | Optimize precursor solution | 06/30/04 | | |
| UOL-1-4 | Determine microstructure/processing relationships | 12/31/04 | | |
| UOL-1-5 | Design full-scale reactor | 09/30/05 | | |
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## TECHNICAL HIGHLIGHTS

We have begun design of a sub-scale turbine blade coating system. The planned CVD system will be a step beyond the 3 cm coupon-scale system used for previous studies and will serve to test techniques for scale-up toward the ultimate goal of a full-size 40 cm x 12 cm turbine blade. Design issues include control of precursor vapor flow over the larger, non-symmetrical surface, uniform heating for two-sided coating and precursor/solvent selection. 3-D computer modeling will be used to evaluated candidate design features before construction.

Previous experiments have used two different precursor/solvent combinations: a mixture of Zr(tmhd) and Y(tmhd) in tetrahydrofuran (THF) and a mixture of zirconium n-butoxide in butanol (76%) and yttrium n-butoxide in toluene (0.5M). While the latter precursor solution produced higher deposition rate it also had clogging problems in the inlet nozzle and produced greater amounts of powder by-product in the exhaust regions. Several other precursors have been identified for future testing. Before using these in actual CVD experiments they will be tested for solubility limit in various solvents, stability in handling and for vapor pressure.

## ISSUES

None.

| **Report Prepared By** | **Date** |
|---|---|
| Thomas L. Starr | 10/16/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ANL-4 | ANL–4: Corrosion and Mechanical Properties of Materials in Combustion and Mixed–Gas Environments | 49640 | 10/01/74 | 09/30/05 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Argonne National Laboratory<br>9700 S. Cass Ave.<br>Argonne, IL 60439 | K. Natesan |

## BUDGET AND COST REPORT

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Prior Year Funds [$K]** | | | | | | | | | | | | |
| **Total Current Year Commitment $K]** | | | 175 | | | | | | | | | |
| **Projected Current Year Costs [$K]** | | | 175 | | | | | | | | | |
| | **O** | **N** | **D** | **J** | **F** | **M** | **A** | **M** | **J** | **J** | **A** | **S** |
| **Planned Costs** | 15 | 29 | 44 | 48 | 63 | 77 | 92 | 106 | 121 | 139 | 155 | 175 |
| **Actual Costs** | 7 | 7 | 10 | 11 | 14 | 15 | 42 | 50 | 74 | 86 | 96 | 109 |
| **Variance** | 8 | 22 | 34 | 37 | 49 | 62 | 50 | 56 | 47 | 53 | 59 | 66 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ANL 4-1 | Continue corrosion evaluation of advanced steam cycle materials in the presence of alkali sulfate/alklai chloride | 06/30/03 | | |
| ANL 4-2 | Continue the hot corrosion studies of Mo-silicide and composite materials at temperatures in the range of 600-800°C | 09/30/03 | | |
| ANL 4-3 | Continue corrosion tests on advanced nickel base alloys in the presence of sulfate deposits at temperatures between 650 and 800°C | 09/30/03 | | |
| ANL 4-4 | Evaluate the corrosion performance of metallic and ceramic materials exposed in NETL and North Dakota coal combustors | 09/30/03 | | |
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## TECHNICAL HIGHLIGHTS

ANL-4 Corrosion and Mechanical Properties of Materials in Combustion and Mixed-Gas Environments

During this period, corrosion testing is continued on several Ni-base alloys in the presence of coal-ash in support of advanced steam-cycle conditions. Experiments were completed at 650 and 800°C. Two ash chemistries that included ash constituents, alkali sulfates and NaCl were used in the experiments. All of the specimens (a total of 44 specimens) exposed at the two temperatures were mounted in metallographic mounts and polished. Optically examination of the specimens is currently in progress. Runs at 725°C are in progress. We have taken slivers of each specimen after 925-h and 1008-h exposures to Ash 1 and Ash 3, respectively, for metallographic examination. Exposure of the remaining specimens is being continued to accumulate more time.
Corrosion study on specimens of Fe-base alloys, that were exposed for a period of time ranging from 336 to 1680 h in the presence of simulated coal ash containing 10 wt.% of $Na_2SO_4$ and $K_2SO_4$ in the ratio of 1:1 and with additions of 1% NaCl, was completed. After each exposure period, the specimens were retrieved and cleaned of the ash and weighed. Subsequently the exposures were continued with the specimens but in the presence of fresh ash addition. All of the exposures were performed in a flowing gas environment that has a composition of air plus 1 vol.% $SO_2$. The alloys selected for the tests included HR3C, HR120, Save 25, NF709, modified 800, 347 stainless steel, HCM12A, Fe3Al clad 304, 671 clad 800H, and 310TaN.

Several of the specimens (from different runs) were examined in detail to evaluate their performance from the standpoint of scaling, internal penetration, corrosion product chemistry and phases. The results were compared with earlier-developed data on alloys exposed to coal ash/alkali sulfate mixture that contained 5 wt.% NaCl.

The corrosion test results on both Fe- and Ni-base alloys was presented at the 17th Annual Fossil Energy Meeting in Baltimore, April 22-24, 2003. A complete manuscript, describing the experimental results and data analysis, was published at the NETL website.

During this period, we received additional material of several Fe-base alloys from NETL. These ring specimens are being cut into coupons for performing corrosion experiments in coal-ash environments and possibly in a steam atmosphere.

## ISSUES

| Report Prepared By | Date |
|---|---|
| K. Natesan/W. A. Ellingson | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| FW-2 | Fireside Corrosion Testing of Canaditate Superheater Tube Alloys, Coatings and Claddings- phase III | 85X-SM-401C | 11/18/93 | 03/31/04 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Foster Wheeler Developement Corporation<br>12 Peach Tree Hill Road<br>Livingston, New Jersey 07039 | G. J. Stanko |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 242 |
| **Total Current Year Commitment $K]** | 242 |
| **Projected Current Year Costs [$K]** | 85 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 23 | 27 | 31 | 43 | 55 | 57 | 59 | 65 | 67 | 69 | 83 | 85 |
| **Actual Costs** | 23 | 4 | 4 | 9 | 15 | 11 | 6 | 2 | 12 | 21 | 8 | 24 |
| **Variance** | 0 | 23 | 27 | 34 | 40 | 46 | 53 | 63 | 55 | 48 | 75 | 61 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| 1.1 | Procure Materials | 03/01/00 | 03/01/02 | 03/01/02 |
| 1.2 | Design Probe | 09/01/00 | 04/15/02 | 04/15/02 |
| 1.3 | Manufacture Probe | 11/01/00 | 02/28/03 | 02/28/03 |
| 1.4 | Install Probe in Boiler | 12/02/00 | 05/15/03 | 06/28/03 |
| 1.5 | Removal and Analysis of 4,000 hour Probe | 10/01/01 | 11/15/03 | |
| 3.1 | Removal and Analysis of 12,000 and 16,000 hour Probe | 12/01/02 | 05/30/05 | |
| 3.2 | Final Report | 03/31/03 | 06/30/05 | |
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## TECHNICAL HIGHLIGHTS

October-December 2002--All the machining of the test coupons has been completed and all the thermocouples and other probe supplies have been procured. The trial welding of the various materials has been performed,

February 2003--The two corrosion probes have been fabricated. We are trying to get the air lines and communication lines modified at the Gallatin Steam plant so we can install the corrosion probes.

June 2003 --The two air cooled corrosion probes were installed in the TVA's Gallatin station One is positioned int he waterwall area of the superheater furnace and one is positioned in the waterwall area of the reheater furnace. The temperature bands for both are 1800-2000 °F.

July-September 2003 -- The two probes were in service for approximately 350 hours within the asigned temperature range of 1800-2000°F. At approximately 360 hours a fusion-welded joint between a wrought and an ODS alloy failed at the HAZ of the ODS alloy. Both probes fell into the boiler; subsequently only one was recovered. Examination of the recovered probe at the lab revealed cracking in the HAZ of all of the ODS alloys. This suggests that fusion welding is not a viable joining process for fabricating the probe. Alternate joining processes are being discussed (with E.W.I.), but none look promising at this time. As a result, consideration is being given to a mechanical restraint that would prevent the probe from falling into the boiler should we be limited to a fusion-welded design. This would require a material with good strength and high-temperature oxidation resistance. Materials were ordered for the fabrication of new probes, but work has not commenced because we haven't finalized a joining method as of yet.

## ISSUES

The end date for the contract will have to be extended or the exposure times for the three probes will have to be revised.
* New joining process needs to be devised because of problems with fusion-welding to ODS alloys.

| Report Prepared By | Date |
|---|---|
| G. J. Stanko | 10/10/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-4A | Corrosion protection of ultrahigh temperature metallic alloys | | | |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| ORNL | M.P. Brady and P.F. Tortorelli |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 18 |
| Total Current Year Commitment $K] | 186 |
| Projected Current Year Costs [$K] | 202 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 15 | 30 | 40 | 60 | 80 | 100 | 125 | 150 | 170 | 180 | 190 | 202 |
| Actual Costs | 9 | 21 | 37 | 50 | 70 | 89 | 110 | 122 | 135 | 146 | 160 | 189 |
| Variance | 7 | 9 | 3 | 10 | 10 | 11 | 15 | 28 | 35 | 34 | 30 | 13 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| 2D/4A 1 | Evaluate corrosion behavior of multi-phase Cr-rich alloys in coal combustion, sulfidation and other aggressive high-temperature | 05/30/03 | | 05/30/03 |
| 2D/4A 2 | 4. Submit a journal paper and/or invention disclosure describing the Cr2Ta-reinforced Cr(Fe) matrix alloys | 07/30/03 | | 09/30/03 |
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## TECHNICAL HIGHLIGHTS

Note: The technical aspects of 2D and 4A are linked. Therefore, the technical highlights are shared between the two efforts.

A patent disclosure "Tough, High-Strength Dual Phase Cr-rich alloys" was submitted in the fourth quarter of FY 03, and meets milestone 2D/4A-2. This disclosure covers the family of castable, Laves-phase strengthened Cr(Fe)-rich matrix alloys with room-temperature fracture toughness in the range of 20 MPa-m1/2 and tensile strength in the range of 250-400 MPa at 1000C. The alloys also exhibit good high-temperature oxidation resistance in air and are resistant to the rapid Cr-nitride subscale formation that limits the use of most Cr-rich alloys in high temperature environments containing nitrogen (e.g. air). It is anticipated that these alloys will offer an attractive alternative to ceramics in high-end specialty component applications in aggressive environments such as thermowells, brackets, dies, and valves. This invention disclosure is the culmination of the Cr-related development efforts, which comes to a close in FY03. The program will be transitioned in FY04 to efforts devoted to intermetallic-strengthened ferritic and austenitic alloys for applications above 650°C, such as superheater tubes, and to design approaches to control oxidation reactions for protection in aggressive high temperature environments, as well as a new route to functional surface synthesis.

## ISSUES

Note that the carryover of 18K to FY03 was required to accommodate costs associated with a post-doctoral fellow that was hired at the end of FY02 (50% time on this Fossil effort).

| Report Prepared By | Date |
|---|---|
| MP Brady | 10/03/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| UNDEERC-4 | Support Services for Ceramic Matrix Composites | 19X-SS112V | 10/01/94 | 10/31/03 |


**Performer Name and Address**

Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

**Principal Investigator(s)**

John Hurley
Charlene Crocker


## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 0 |
| **Total Current Year Commitment $K]** | 64 |
| **Projected Current Year Costs [$K]** | 64 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 5 | 10 | 16 | 21 | 26 | 32 | 37 | 42 | 48 | 53 | 58 | 64 |
| **Actual Costs** | 0 | 0 | 2 | 3 | 3 | 2 | 6 | 9 | 6 | 1 | 4 | 6 |
| **Variance** | 5 | 10 | 14 | 18 | 23 | 30 | 31 | 33 | 42 | 52 | 54 | 58 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| UND-4-2 | Expose coupons in EERC systems and perform ASTM corrosion determinations and SEM analysis | 09/30/03 | 10/31/03 | |
| UND-4-3 | Give presentation at the Seventeenth Annual Conference on Fossil Energy Materials | 04/30/03 | | 04/30/03 |
| UND-4-4 | Prepare final report | 10/31/03 | | |
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## TECHNICAL HIGHLIGHTS

The University of North Dakota Energy & Environmental Research Center (EERC) is providing expertise and assistance to Advanced Research Materials Programs investigating ceramic and alloy corrosion in fossil energy systems. It is difficult to simulate under controlled laboratory conditions all of the possible corrosion and erosion mechanisms to which a material may be exposed in an energy system. Therefore, the EERC is working with Oak Ridge National Laboratory (ORNL) to provide materials scientists with opportunities to expose materials in pilot-scale systems to conditions of corrosion and erosion similar to those occurring in commercial power systems.

The EERC has two pilot-scale solid fuel-fired systems available for exposure of material coupons. The slagging furnace system (SFS) is a high-temperature combustor built under the U.S. Department of Energy High Performance Power System Program as a testing facility for advanced heat exchanger subsystems. In addition, a pilot-scale entrained-bed gasifier system known as the transport reactor development unit (TRDU) is available in which coupons can be exposed and hydrogen separation membranes tested under field conditions.

An oxygen-enriched combustion test was completed in the SFS in July under separate DOE funding. It was fired on natural gas and Illinois No. 6 coal. Conditions in the SFS simulated those in an indirectly fired combined-cycle (IFCC) design. Because of its high efficiency, an IFCC system is the most appropriate power concept for employing oxygen-enriched combustion. Five different types of alloy coupons were installed in the SFS prior to the test. The convective pass sample coupons included three new alloy samples from ORNL and two new samples from Ames Laboratory. One of the samples from ORNL contain Cr with Fe, Ta, Mo, Ti, and Si, and the second and third samples contain Cr with Ta, Mo, Si, La, and Ti. The two samples from Ames Laboratory are Ni, Cr, Al, and Fe hot-gas filter candidate materials spot-welded into a ring. In addition to the convective pass samples, duplicate samples of the Ames materials were installed in the heat exchanger elbow. All of the coupons were exposed to 100 hours of natural gas firing and 8 ¾ hours of coal firing. During the natural gas firing, the samples in the convective pass were heated to an average of 920°C, whereas those samples in the heat exchanger elbow reached only 600°C. Average gas compositions during natural gas firing were 5% $O_2$, 29% $CO_2$, 45% $H_2O$, and 47 ppm NOx, and 0% $SO_2$ with a balance of $N_2$. During the 8 ¾ hours of coal firing, the average temperatures remained the same in both areas. Average gas composition during coal firing was 4% $O_2$, 46% $CO_2$, 23% $H_2O$, 253 ppm NOx, and 1821 ppm $SO_2$ with a balance of $N_2$. The relatively large amounts of $N_2$ in the flue gas occurred because of leakage of air into the negative pressure combustion system. After testing, the ORNL alloys were dark gray to nearly black and covered with a dark brown ash deposit. The coupons were cleaned and will be reinstalled in the SFS during the next coal-fired test. The Ni, Cr, Al, and Fe alloy samples from Ames Laboratory were a slightly darker shade of gray and also covered with a dark brown ash deposit. The two from the heat exchanger elbow were covered with a finer, lighter ash. No corrosion was visible on any of the samples. Those from Ames Laboratory were returned there for analysis and further testing. Two biomass–coal-cofired combustion tests are scheduled for the SFS in October and November 2003.

## ISSUES

None.

| Report Prepared By | Date |
|---|---|
| John Hurley | 10/16/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| INEEL - 2 | INFLUENCE OF PROCESSING ON MICROSTRUCTURE AND PROPERTIES OF IRON ALUMINIDES AND COATINGS | | 10/01/85 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Idaho National Engineering and Environmental Laboratory<br>BWXT, LLC<br>P.O. Box 1625<br>Idhao Falls, ID 83415 | Richard N. Wright |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 4 |
| **Total Current Year Commitment $K]** | 179 |
| **Projected Current Year Costs [$K]** | 150 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 2 | 4 | 5 | 9 | 13 | 17 | 34 | 59 | 85 | 115 | 135 | 150 |
| **Actual Costs** | 2 | 4 | 5 | 9 | 13 | 17 | 26 | 56 | 68 | 80 | 95 | 113 |
| **Variance** | 0 | 0 | 0 | 0 | 0 | 0 | 8 | 3 | 17 | 35 | 40 | 37 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| INEEL-2-1 | Characterize Residual Stress as a Function of Thickness and Composition for High Al Fe-Al Coatings | 06/30/03 | 08/30/03 | |
| INEEL-2-2 | Relate Thermal Spray Parameters to Microstructure, Stress and Oxidation Resistance | 09/30/03 | 11/30/03 | |
| INEEL-2-3 | Determine Microstructure/Property Relationships for Chromia Formers | 09/30/04 | | |
| INEEL-2-4 | Develop Processing Methods to Mitigate Residual Stress | 09/30/04 | | |
| | | | | |
| | | | | |
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## TECHNICAL HIGHLIGHTS

A wide range of iron aluminide alloy compositions have been applied by thermal spray onto steel substrates and the residual stress measured by both curvatrure analysis and x-ray diffraction. Using careful calibration standards and a finite element model that considers both elastic and plastic processes, the development of residual stress through the thickness of the coating has been determined. By seperating the coating stress from the bending induced strains for thin substrates it has been possible to accurately relate the total residual stress to the process parameters for deposition at a wide range of particle velocities at a fixed temperature. Further, it has been demonstrated that the stress arises from both quenching and particle peening. These influences respond quite differently to particle velocity and are ammeanble to control through control of the spray parameters. Two manuscripts for peer reviewed papers have been submitted during this quarter as a result of this work. One paper on residual stress measurements in Mo-Si intermetallics and on coatings near FeAl composition was submitted. The second details a method to calculate the individual contributions to total residual stress in Fe3Al and stainless steel (used as a model system) coatings.

Development of methods and equipment has begun for testing of FeAl and Mo-Si coatings in well controlled elevated temperature environments designed to simulate fossil plant conditions has begun. Both oxidizing and sulfidizing contitions will be examined, as well as coupons with simulated ash deposits. The thermal cycle will be controlled independent of the envrionmental conditions. Characterization of the microstructure, flexural strength and adhesion of coatings deposited using two different deposition velocities with nominally constant deposition temperature has been completed for baseline comparisons.

Thermal cycling experiments have shown that minimum total residual stress gives rise to the best coating performance in thermal cycling in an oxidizing environment. This is in contrast with commonly held belief in the industry that compressive stress yeilds better performance. Large compressive stresses correlate with coating failure by fracture and spallation between coating layers parallel to the substrate/coating interface. Coatings with large tensile stresses also fail after relatively few thermal cycles, however, the failure in these coatings occurs by debonding of the coating from the substrate. Numerical simulation of brittle materials, as the iron aluminides tend to be in the thermal spray coatings, has indicated that large compressive stresses in the plane of the coating can in fact give rise to cracking parallel to the interface. It is not likely that such a failure mechanism would be observed for ductile compositions. It is probably signigicant for most classes of coatings designed for high temperature coal combustion conditions.

## ISSUES

The spending rate and schedule of this project continue to be impacted by the late arrival of FY'03 funds; note that the year end spending does not reflect $30K for an uncosted obligation for a TGA system to be used in coating evaluation in coal combustion atmosphere testing.

| Report Prepared By | Date |
|---|---|
| Richard N. Wright | 10/16/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-2(E) | ODS Alloys | | | |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| ORNL | I. G. Wright |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | (3) |
| Total Current Year Commitment $K] | 217 |
| Projected Current Year Costs [$K] | 217 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 18 | 36 | 54 | 72 | 90 | 109 | 127 | 145 | 163 | 181 | 199 | 217 |
| Actual Costs | 14 | 31 | 41 | 55 | 65 | 74 | 94 | 114 | 142 | 166 | 184 | 215 |
| Variance | 4 | 5 | 13 | 17 | 25 | 35 | 33 | 31 | 21 | 15 | 15 | 2 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ORNL-2(E)-16 | Initiate characterization of effects of pre-consolidation processing on microstructure of new ODS-FeCrAl, and quantification of the influence on creep | 01/31/02 | 05/31/04 | |
| ORNL-2(E)-17 | Initiate characterization of effects of post-consolidation processing on microstructure of new ODS-FeCrAl, and quantification of the influence on creep | 03/31/02 | 09/30/04 | |
| ORNL-2(E)-21 | Initiate testing to quantify the relationship between the parameters influencing torsional strain and modification of the alloy recrystallization behavior | 01/31/03 | 01/31/04 | |
| ORNL-2(E)-22 | Characterize the effects of pre-consolidation procedures to commercially-produced ODS-FeCrAl alloy powder | 05/31/03 | 05/31/04 | |
| ORNL-2(E)-23 | Prepare a technical paper describing the oxidation life prediction model | 09/30/03 | 11/15/03 | |
| ORNL-2(E)-24 | Initiate flow-forming trials using revised processing parameters | 12/31/03 | | |
| ORNL-2(E)-25 | Initiate environmental testing of joints | 05/31/04 | | |
| ORNL-2(E)-26 | Collect, analyze, and compile results from joining trials | 08/31/04 | | |
| | | | | |

## TECHNICAL HIGHLIGHTS

Joints have been made in unrecrystallized MA956 tubes (produced at ORNL) using a commercial inertia-welding machine, and the microstructures following recrystallization have been examined. The results have been discussed with the inertia-welding vendor, and joining conditions devised to produce an improved microstructure. Further trials will be conducted.

Processing of tubes of MA956 in a commercial pilgering machine to produce different degrees of deformation (flow-forming) led to the development of modified alloy grain structures with, in some cases, a decrease in the length-to-diameter ratio of the grains, which is considered desirable for improved hoop strength--one of the main targets for improving the properties of ODS alloy tubing. Samples showing the most promising microstructures have been slit and flattened to allow creep tests to be run in the transverse (hoop) direction; tests are in progress to compare the creep behavior in the hoop and longitudinal directions with those of tubes produced by standard processing.

Detailed examination of parallelepiped- and disc-shaped specimens of MA956 oxidized to failure has indicated that, in the absence of gross scale loss by spallation, the Al content of the alloy (the element needed to form and maintain the protective oxide scale) is essentially totally consumed, and that some further protection is provided by the Cr content of the alloy before breakaway oxidation occurs, signalling end of service life. In the elongated parallelepiped shape, however, preferential, and apparently continuous scale spallation from corners led to the development of a concentration gradient in Al and early failure in those locations. The reasons for this behavior have implications for practical component design, as well as for the approach used for modelling oxidation-limited lifetime. A procedure for generating an 'average' value of an important modelling parameter--CBb, the maximum Al content which leads to the initiation of breakaway oxidation--from standard oxidation kinetic data was also shown to provide an improved lifetime prediction for elongated parallelepiped shapes. These data have been incorporated into a draft technical paper.

## ISSUES

ORNL-2(E)-16, 17 and 22: these milestones remain in abeyance since the target supplier of material, Special Metals Corp., remains under Chapter 11 restrictions. The disposition of SMC's ODS alloy business has not been finally resolved, and attempts to obtain processed alloy powder from SMC have not been successful. The price quoted by the only alternative supplier, Metallwerk Plansee GmbH, to produce a batch of ODS-FeCrAl powder was beyond the funding available to this program.

ORNL-2(E)-21 was stalled as a result of relocation of the equipment as part of a laboratory modernization effort, and the retirement of key personnel. Arrangements have been made for priority use of this equipment as soon as it is reinstalled.

| **Report Prepared By** | **Date** |
|---|---|
| Ian G. Wright | 10/15/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| UCSD-2 | Oxide Dispersion Strengthened Fe3Al Based Alloy Tubes: Application Specific Development for Power Generation Industry | 19X-SY09C | 12/08/97 | 01/07/04 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Department of Structural Engineering<br>University of California, San Diego<br>9500 Gilman Drive, 0085<br>La Jolla, CA 92093 | Bimal K. Kad |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 305 |
| **Total Current Year Commitment $K]** | 45 |
| **Projected Current Year Costs [$K]** | 75 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 305 | 305 | 305 | 305 | 305 | 305 | 305 | 350 | 350 | 350 | 350 | 350 |
| **Actual Costs** | 249 | 253 | 256 | 262 | 267 | 269 | 270 | 272 | 276 | 280 | 293 | 294 |
| **Variance** | 56 | 52 | 49 | 43 | 38 | 36 | 35 | 78 | 74 | 70 | 57 | 56 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| 1.1 | Base ODS-Powders, alloy chemistry, Fe/Al ratio, alloy additions Dispersoids: chemistry, matrix compatibility | 06/30/02 | | 06/30/02 |
| 1.2 | FAS compositions, scale and distributions for functionally gradient tubes | 09/30/02 | | 12/31/02 |
| 2.1 | Milling process optimization, powder strain state characterization | 12/31/02 | 03/31/03 | 03/31/03 |
| 2.2 | primary extrusion consolidation: process parameters for tubes & sheet processing; Explore functionally gradients sheets & tubes | 12/31/02 | 06/30/03 | 06/30/03 |
| 2.3 | initial material strength, texture and anisotropy evaluation | 03/31/03 | 06/30/03 | 06/30/03 |
| 2.4 | Static Recrystallization Kinetics of task 2.2 and materials | 06/30/03 | 09/30/03 | 09/30/03 |
| 2.5 | Gradient Recrystallization schemes of task 2.2 materials | 06/30/03 | 09/30/03 | 09/30/03 |
| 3.1 | Mechanical strength: uniaxial and biaxial loading assessmen | 09/30/03 | 12/31/03 | |
| 3.2 | Creep Performance: longitudinal and transverse loading assessment | 12/31/03 | | |

## TECHNICAL HIGHLIGHTS

CREEP TESTING: Hoop Creep of ODS-Fe3Al Alloy Tubes

Long duration creep-life evaluation and stress-rupture testing is being performed on four creep-testing rigs (maximum test temperature = 1200degC) installed at UCSD during the course of this research program.

Test matrices are currently examining the threshold stress capabilities of transversely oriented specimens. Transverse creep specimens are being extracted from as-extruded 1-3/8" OD tubes as follows: the tubes are split along their length by wire EDM, and then hot press-forged (single step) flat and/or rolled flat at 900degreesC. ASTM E-8 specimens are then spark machined from the forged piece. The machined test specimens are then subjected to a series of high temperature secondary recrystallization heat-treatments (over a range of time temperature combinations in different environments) prior to the incremental stress rupture tests. At the outset the bulk of the tests are conducted in air in the 900 - 1000 degrees C temperature range.

A threshold stress of 2ksi has been recorded for PMWY-3 chemistry in creep tests conducted at 1000 degrees C. These samples were recrystallized in an inert argon atmosphere. The strain vs. time plots indicated an initial transient creep rate of 3e-4/day followed by a steady state creep rate of 1e-4/day. The test is continuing (as of 10/17/03) with over 3900 hours of exposure in air. This 2ksi threshold is also observed in cross-rolled ODS-Fe3Al samples (15-25% thickness reduction).

A threshold stress of 6ksi has been recorded for tests conducted at 900 degrees C. The argon recrystallized as well as the cross-rolled and air recrystallized specimens failed at the 6ksi stress level following a 516hours and 523 hours exposure, respectively. The strain vs. time plots show a range of steady state creep rates depending on the specifics of thermal-mechanical treatment. For example the rate is 3e-5/day in regular extruded tubes, but is an order of magnitude lower (3e-6/day) in cross-rolled ODS-Fe3Al specimens (15-25% thickness reduction). Both tests were run with a 1ksi stress increment after 1000hours at each stress level, i.e., each test survived a 1000hour exposure at 5ksi level. Repeat tests are now being conducted at a fixed 5ksi stress - and no failure has been observed (as of 10/17/03) after 3600 hours of exposure in air.

NON FUSION JOINING of MA956 TUBES

Recent efforts include inertia welding of ODS-alloy tubes to validate this technology for possible end-use applications. Initially MA956 tubes have been used to produce robust butt configuration joints in 2-1/2" OD -1/4" wall thickness tubes. Initial bend test indicate no loss of strength in the joint region. Optical microstructures reveal a 2-3mm region (along the tube axis) of intense material flow at the joint interface. The initial longitudinal grain structure is bent outwards at the inner and outer periphery, but tends to run along the hoop direction in the middle of the tube wall. Mechanical properties have been examined in the as-welded state as well as after recrystallization treatment. Tensile tests of as-welded materials indicate that sample fails at the joint interface at about 90-95% of the matrix yield strength with low ductility. However, in recrystallized specimens the matrix fails after significant ductility. TEM examinations reflect the fine grained nature of the joint region which is unchanged after the recrystallization treatment.

Creep Testing: MA956 Joints

Longitudinal sections were cut (with the joint region well within the sample gage length) and tested in air at a constant load (2ksi initial stress) over the 700-900degC range. The sample failed upon loading (life = 2.4hrs) at 900degC. At 800degC the test lasted 128 hours. At 700degC negligible strain was recorded after 200 hours and this test is continuing presently at higher levels of stress. The creep rates observed (in the order of increasing temperature) are 4e-5, 3.8e-3 and 4e-1 respectively. The steady-state creep rate vs. temp. (or 1/T) is linear which yields an activation energy of the order of 437kJ/mole. We note that the activation energy is much larger than the activation energy of self diffusion of iron (289kJ/mole in alpha-iron, 293kJ/mole in gamma-iron). Literature suggests this is to be expected in dispersion strengthened alloys which exhibit a high stress exponent (i.e. n>5). More work is continuing to establish a firm stress threshold.

## ISSUES

| Report Prepared By | Date |
|---|---|
| Bimal K. Kad | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| UL-2 | Reduction of Defect Content in ODS Alloys | 1DX-SY382V | 01/01/98 | 12/31/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| University of Liverpool<br>Liverpool<br>L69 3BX<br>United Kingdom | Dr Andy Jones |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 30 |
| **Total Current Year Commitment $K]** | 129 |
| **Projected Current Year Costs [$K]** | 129 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 38 | 38 | 38 | 38 | 38 | 38 | 62 | 62 | 62 | 129 | 129 | 129 |
| **Actual Costs** | 16 | 21 | 25 | 30 | 35 | 55 | 88 | 93 | 98 | 103 | 109 | 113 |
| **Variance** | 22 | 17 | 13 | 8 | 3 | (17) | (27) | (32) | (36) | 26 | 21 | 16 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| SY382v14 | Influence of powder size/condition on oxidation identified | 03/31/02 | | 03/31/02 |
| SY382v15 | Practicable combination of steps identified to reduce powder oxidation during consolidation | 05/31/02 | | 06/30/02 |
| SY382v16 | Development of long-term porosity compared in Fe3Al and PM 2000 | 06/30/02 | 09/30/02 | 09/30/02 |
| SY382v17 | Report on fluidised bed separation of defect MA powders from gas atomised Fe3Al powder beds | 07/31/02 | | 09/30/02 |
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## TECHNICAL HIGHLIGHTS

i) Onset of secondary recrystallisation in warm flow-formed PM2000 tubes

After annealing warm flow-formed PM2000 tubes at 900°C for 1 hour, axially periodic islands of recrystallised material were observed approximately 100mm below the outer surface of the tube. These islands represent the onset of secondary recrystallisation and it was hoped that the pattern of the deformation condition of the tube in this state would elucidate the hoop recrystallisation patterns observed after complete secondary recrystallisation. To date, detailed EBSD studies of the tube's microstructure have revealed no data additional to that already obtained from EBSD of other samples. In fact, there appears to be less clear crystallographic data available from this sample than was obtained from previous samples. It is surmised that the extensive recovery that will have taken place may have obscured previously clear textures and deformation patterns.

ii) Critical strain recrystallisation of PM2000 variants

In order to elevate the recrystallisation temperature of ODS-free regions within the PM2000/Fe variant alloy to more closely match that of the bulk, PM2000 regions, work is underway to superimpose a near critical level of strain on the microstructure of the as-extruded composite prior to recrystallisation annealing of the whole. This has been performed by bending samples of the variant around a former in order to exert a range of strains across the sample thickness. Bending conditions were determined using locally sourced samples of an ODS-free FeCrAl Kanthal alloy. Samples subjected to critical strain annealing have so far demonstrated no clear interaction between recrystallisation in the ODS-free regions and that in the remaining, bulk PM2000.
Further work involving more complex deformation and recrystallisation regimes is underway. It is hoped that the recrystallisation temperature of the ODS-free regions can be elevated while the recrystallisation temperature of the PM2000 is reduced, thus enabling concurrent recrystallisation across both ODS free and PM2000 regions.

iii) Deformation patterns in flow-formed tubes
The axially undulating deformation microstructures seen in longitudinal sections of warm flow-formed tubes deformed by 86% with two roller passes are believed to be due to the periodic tracks of the flow-forming rollers.
No such undulating microstructures have been identified in a warm flow-formed tube deformed 45% in a single pass. The reasons for this are not clear, since two, separate periodicities can be seen in the 'two-pass' tube, so it would be expected that a single periodicity would be present and observable in the single pass tubes.
Samples of the tube were examined in the recovered, partially recrystallised and fully recrystallised condition but no periodic axial microstructures were observed. It is hoped that EBSD work may reveal more and this is the chosen way forward.

## ISSUES

A new statement of work together with the appropriate contract pricing proposal proforma and cover sheet relating to the proposed continuation of the current subcontract work has been submitted through the project officer.

| **Report Prepared By** | **Date** |
|---|---|
| Andy Jones | 10/16/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ANL-1 | Development of Nondestructive Evaluation Methods for Structural and Functional Materials | 49640 | 10/01/74 | 09/30/08 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Argonne National Laboratory<br>9700 S. Cass Ave.<br>Argonne, IL | W. A. Ellingson |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | |
| Total Current Year Commitment $K] | 175 |
| Projected Current Year Costs [$K] | |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 15 | 29 | 44 | 48 | 63 | 77 | 92 | 106 | 121 | 139 | 155 | 175 |
| Actual Costs | 0 | 0 | 0 | 0 | 0 | 0 | 40 | 136 | 175 | 202 | 217 | 229 |
| Variance | 15 | 29 | 44 | 48 | 63 | 77 | 52 | (30) | (55) | (63) | (62) | (54) |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ANL 1-1 | Correlate elastic optical scatter data and luminescence spectrosopy for air-plasma-sprayed TBCs | 01/31/03 | | |
| ANL 1-2 | Conduct synchrotron X-ray microimaging of new H2and O2 membranes | 05/31/03 | | |
| ANL 1-3 | Submit report on microimaging technology and membrane development | 07/31/03 | | |
| ANL 1-4 | Submit report on NDE studies and TBC/bond coat interface | 09/30/03 | | |
| | | | | |
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| | | | | |

## TECHNICAL HIGHLIGHTS

ANL-1: Development of Nondestructive Evaluation Methods for Structural and Functional Materials

The activities this period focus on the two activities addressed under this project. The focus areas are: (1) NDE technology development for thermal barrier coatings for advanced turbines, and (2) NDE technology development for characterizing high temperature gas-separation membranes.

(1) NDE technology development for thermal barrier coatings continued with the University of Pittsburgh, Univ. of Connecticut, Solar Turbines and Praxair Surface Systems. The NDE work at Argonne is focused on development of the laser back scatter method patented by ANL. Work includes efforts with the Univ. of Pittsburgh and focused on use of the laser back scatter NDE method for analyzing electron beam physical vapor deposition (EB-PVD) test samples. As noted in prior reports, the Univ. of Pittsburgh is using a microindentation technique to check the bond strength of the TBC - bond coat interface and to establish parameters for a model for failure. Correlations between the laser back scatter and other methods continued with several new test samples. The data from the laser back scatter continue to be very good and agree exactly with the other destructive data. We continued our cooperative work with Solar Turbines of Caterpillar regarding determination of the thickness of the thermally grown oxide layer (TGO) for air plasma spray TBCs. This period we demonstrated laser scatter correlations with TGO thickness even in the presence of a TBC. The optical coherence tomography system (OCT) installed last quarter was modified and reverse-engineered and is now being retrofitted for TBC thickness measurements. In addition this period, we have ordered the software that will allow us to begin to do modeling for the laser scatter. We hope to have this installed next period.

(2) NDE technology development for high temperature gas separation membranes continued with more extensive work with Ceramatec. Various membrane configurations were received from Ceramatec includeing SYNGAS and Oxygen separation membranes. No work was done with palladium coated oxide tubes for gas separation membranes in cooperation with Los Alamos National Laboratory. As noted last period, we have started to look in terahertz waves for application and interaction with NASA-Langley regarding this effort has started.

Presentations/Meetings Attended

(1) William A. Ellingson presented an invited paper titled " NDE Technology for Risk Reduction of Ceramic Components for Gas Turbines" to the First International Conference on Industrial Gas Turbine Technologies, held July 10-11. 2003, in Brussels, Belgium

(2) William A. Ellingson presented an invited paper titled," Development of an Acousto-Ultrasonic Method for Porous Ceramics" to the 10th International Congress on Sound and Vibration to be held July 7-10, 2003, in Stockholm, Sweden

Presentations/Meetings Planned

(1) W.A. Ellingson has been invited to be a speaker at a forum at the American Society for Nondestructive Testing meeting in Pittsburgh, PA, October 14-17,2003,

(2) W.A. Ellingson plans to visit the Boeing Company nondestructive testing facility in Huntington Beach, CA, October 21, 2003

## ISSUES

| Report Prepared By | Date |
|---|---|
| W. A. Ellingson | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| AR807GA1 | Development of a Commercial Process for the Production of Silicon Carbide Fibrils | XSZ337 | 03/28/00 | 12/01/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| ReMaxCo Technologies, Inc.<br>1010 Commerce Park Drive, Suite I<br>Oak Ridge, TN 37830 | Richard Nixdorf |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 293 |
| **Total Current Year Commitment $K]** | 144 |
| **Projected Current Year Costs [$K]** | 144 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | | | | | 3 | 8 | 10 | 12 | 14 | 40 | 65 | 90 |
| **Actual Costs** | | | | 0 | 3 | 8 | 10 | 12 | 14 | 16 | 17 | 43 |
| **Variance** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24 | 48 | 47 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| AR807GA1-1 | Review Fibril Characterization | 04/01/03 | | 04/01/03 |
| AR807GA1-2 | Improve Pilot Furnace Equipment | 08/01/03 | 12/01/03 | |
| AR807GA1-3 | Establish Volume Production Operation | 10/01/03 | 02/01/03 | |
| AR807GA1-4 | Produce Volume Quantities of Fibrils | 02/01/04 | 03/01/03 | |
| AR807GA1-5 | Fibril Product Evaluation and Final Report | 05/01/04 | 04/01/03 | |
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## TECHNICAL HIGHLIGHTS

1 Contracts have be issued to MS&E to design new gas feed system, RF Technologies to design microwave feed system and reaction vessel fabrication and McCormick Engineering to coordinate the new reaction vessel fabrication and start-up.

2 The ReMaxCo Silicon Carbide Fibril Growth Project was a feature article in Industrial Heating Magazine's August issue.

## ISSUES

ReMaxCo and Microwave Materials Technologies designed and built the first Fibrils demonstration reaction vessel using in-house expertise. The reaction gas feed system and the microwave distribution system were inadequate to produce any volume of quantity Fibril product. ReMaxCo has spent significant time and effort locating experienced industrial experts in these fields to assist in the design and fabrication of the improved reaction vessel. The required companies are now under contract, actively working on the new design. This design quality improvement effort has cost a four month delay in the completion of the new reaction vessel. The additional time requirement will produce a substantially improved Fibrils production unit, with a much higher probability of success.

| **Report Prepared By** | **Date** |
|---|---|
| Richard Nixdorf | 10/14/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| | Novel Processing of Mo-Si-B Intermetallics for Improved Efficiency of Power Systems | W-7405-ENG-82 | 06/01/00 | 09/30/05 |


**Performer Name and Address**

Dr. Patricia Thiel
321 Spedding Hall
Iowa State University
Ames, IA 50011

**Principal Investigator(s)**

Dr. Matthew J. Kramer
Dr. Mufit Akinc
Dr. Andrew J. Thom


## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 61 |
| **Total Current Year Commitment $K]** | 211 |
| **Projected Current Year Costs [$K]** | 185 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 14 | 28 | 41 | 55 | 69 | 83 | 100 | 117 | 134 | 151 | 168 | 185 |
| **Actual Costs** | 13 | 29 | 45 | 61 | 70 | 86 | 102 | 119 | 137 | 153 | 164 | 175 |
| **Variance** | 1 | (1) | (4) | (6) | (1) | (3) | (2) | (2) | (3) | (2) | 4 | 10 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| | Thermal barrier coating development | 01/30/04 | | |
| | Alloy oxidation in synthetic combustion atmosphere | 04/30/04 | | |
| | Nb-Mo-Si-B alloy development | 07/30/04 | | |
| | Control of low temperature catastrophic oxidation | 09/30/04 | | |
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## TECHNICAL HIGHLIGHTS

Progress has been made on the first three milestones for FY04 and will be discussed below.

Thermal barrier coating development

Powder for thermal spraying was sent to INEEL. We are in the process of evaluating the use of Mo foil as a substrate for spray-deposited Mo-Si-B alloys. One side of the foil will be sprayed with Mo-rich Alloy 3, while the other side will be sprayed with Si-rich Alloy 1. The sandwich structure will then be annealed at elevated temperature in inert atmosphere to evaluate the microstructural/phase stability of the coatings. Annealing in air will show the oxidative stability of the individual coatings and their ability to protect the oxygen sensitive Mo foil.

Alloy oxidation in synthetic combustion atmosphere

Previous work has shown that the Mo-rich Alloy 3 is susceptible to enhanced oxidation in wet air. In order to better understand the role that water plays in the degradation process, we have oxidized the alloy in wet nitrogen. This revealed a somewhat unexpected result that the alloy fails to macroscopically passivate as the alloy continues to lose mass at a large rate of about 1.7 mg/cm2/hr over the entire test duration of about 100 hours. This is in contrast to the wet air exposures that show a macroscopic passivation based on mass loss rates of about three orders of magnitude lower. Thermodynamic modeling of the loss process in wet nitrogen predicts the formation of a Mo2N intermediate phase as an important step in the conversion of alloy Mo into a volatile MoO3 phase. For water vapor to act as the oxidant in this process, measurable amounts of hydrogen must be produced, and we are currently attempting to verify this through mass spectrometry measurements of the effluents from the oxidation process. We are also starting oxidation experiments of Alloy 3 in wet argon to alternately assess whether Mo2N formation is necessary. We will also investigate the Si-rich Alloy 1 under similar conditions to assess whether this increased mass loss behavior occurs. Thermodynamic modeling predicts that the Mo2N intermediate phase formation is much more favorable in the silicide phases, suggesting that Alloy 1 would be even more susceptible than Alloy 3 to the accelerated and continuous loss of Mo.

Nb-Mo-Si-B alloy development

Work has started on designing a process to selectively remove the Nb2O5 component from the mixed oxide scale that forms when the quaternary alloy is oxidized in air. The hypothesis is that by removing the fast growing pentoxide component from the scale, the remaining borosilicate glass in the scale can then form a continuous scale that can protect the underlying alloy in a manner similar to that of the ternary Mo-Si-B alloy. The advantage of the quaternary alloy is the ability to form the bcc-metal (Nb,Mo) phase in coexistence with a quaternary T1-like silicide phase. The process being considered is a chlorination reaction in which the Nb2O5 component is converted into a volatile NbCl5 phase in the presence of a mixed chlorine and carbon monoxide gas atmosphere. Because of the corrosive and toxic nature of these gases, the Safety Review Committee must thoroughly review this proposed activity. Once the chlorination process design is approved, we expect to quickly complete its construction and begin testing.

## ISSUES

The postdoctoral scientist working on the project concluded his employment on 7/30/03. He has been replaced by a high quality graduate student that wishes to pursue a doctoral degree.

| **Report Prepared By** | **Date** |
|---|---|
| Andrew J. Thom | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-2D | Intermetallic Reinforced Cr Alloy | | | |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| ORNL | M.P. Brady and C.T. Liu |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 4 |
| Total Current Year Commitment $K] | 109 |
| Projected Current Year Costs [$K] | 113 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 8 | 16 | 24 | 34 | 45 | 55 | 70 | 85 | 95 | 100 | 105 | 113 |
| Actual Costs | 7 | 12 | 19 | 28 | 37 | 42 | 63 | 72 | 79 | 85 | 92 | 102 |
| Variance | 1 | 4 | 6 | 7 | 8 | 13 | 7 | 13 | 16 | 15 | 13 | 11 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| 2D/4A 1 | Evaluate corrosion behavior of multi-phase Cr-rich alloys in coal combustion, sulfidation and other aggressive high-temperature | 05/30/03 | | 05/30/03 |
| 2D/4A 2 | Submit a journal paper and/or invention disclosure describing the Cr2Ta-reinforced Cr(Fe) matrix alloys | 07/30/03 | | 09/30/03 |
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## TECHNICAL HIGHLIGHTS

Note: The technical aspects of 2D and 4A are linked. Therefore, the technical highlights are shared between the two efforts.

A patent disclosure "Tough, High-Strength Dual Phase Cr-rich alloys" was submitted in the fourth quarter of FY 03, and meets milestone 2D/4A-2. This disclosure covers the family of castable, Laves-phase strengthened Cr(Fe)-rich matrix alloys with room-temperature fracture toughness in the range of 20 MPa-m1/2 and tensile strength in the range of 250-400 MPa at 1000C. The alloys also exhibit good high-temperature oxidation resistance in air and are resistant to the rapid Cr-nitride subscale formation that limits the use of most Cr-rich alloys in high temperature environments containing nitrogen (e.g. air). It is anticipated that these alloys will offer an attractive alternative to ceramics in high-end specialty component applications in aggressive environments such as thermowells, brackets, dies, and valves. This invention disclosure is the culmination of the Cr-related development efforts, which comes to a close in FY03. The program will be transitioned in FY04 to efforts devoted to intermetallic-strengthened ferritic and austenitic alloys for applications above 650°C, such as superheater tubes, and to design approaches to control oxidation reactions for protection in aggressive high temperature environments, as well as a new route to functional surface synthesis.

## ISSUES

| Report Prepared By | Date |
|---|---|
| MP Brady | 10/03/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-2(I) | Mo-Si Alloy Development | FEAA028 | 10/01/02 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>P.O. Box 2008<br>Oak Ridge, TN 37831 | J. H. Schneibel |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 7 |
| Total Current Year Commitment $K] | 142 |
| Projected Current Year Costs [$K] | 142 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 11 | 22 | 34 | 46 | 58 | 70 | 82 | 94 | 106 | 118 | 130 | 142 |
| Actual Costs | 8 | 23 | 33 | 45 | 60 | 71 | 93 | 108 | 99 | 106 | 110 | 129 |
| Variance | 3 | (1) | 1 | 1 | (2) | (1) | (11) | (14) | 7 | 12 | 20 | 13 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| ORNL-2(I)-1 | Examine the influence of Si3N4 additions on the oxidation resistance of Mo-Si-B alloys | 03/31/03 | | |
| ORNL-2(I)-2 | Examine oxidation-resistant coatings such as MoSi2 on Mo-Si-B alloys | 09/30/03 | | |
| ORNL-2(I)-3 | Examine effects of Al and AlN on the oxidation resistance of Mo-Si-B alloys | 03/31/04 | | |
| ORNL-2(I)-4 | Fabricate light-weight Mo-Nb-Si-B alloys consisting of alpha-Mo, (Mo,Nb)5Si3, and (Mo,Nb)5SiB2 and assess their strength and oxidation resistance | 09/30/04 | | |
| ORNL-2(I)-5 | Ductilize molybdenum by incorporating suitable spinel or oxide particles and determine the ductile-to-brittle transition temperature | 03/31/05 | | |
| ORNL-2(I)-6 | Fabricate molybdenum with the aim to optimize oxidation resistance and ductility at the same time | 09/30/05 | | |
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## TECHNICAL HIGHLIGHTS

Two sets of Mo-Si-B alloys with continuous Mo solid solution matrices were prepared vacuum annealing of powders followed by hot isostatic pressing. The first alloy was prepared from Mo-20Si-10B (at.%) powder with initial sizes ranging from 90 to 180 micron. Its Mo solid solution volume fraction was 17%. Specimens were sent to R. O. Ritchie at Lawrence Berkeley National Laboratory, where their crack propagation behavior will be studied. The second alloy was fabricated from Mo-20Si-10B powder with initial sizes ranging from 45 to 90 micron. Its Mo solid solution volume fraction was 13%. Its oxidation resistance will be investigated in the Corrosion Science and Technology Group at ORNL.

The preparation of Mo-coated Mo-Si-B powders via Si evaporation (as Si and SiO) suffers from the difficulty of measuring the volume concentration of the Mo solid solution phase in the powders. X-ray examination of the vacuum-annealed powders as-is gives misleading results, because the limited penetration of the x-rays means that the x-rays negotiate mostly the Mo-rich surface of the particles. In order to avoid this problem, the powders were ground to a much finer size in order to provide a statistically meaningful evaluation of the Mo-phase. For reasons that are not well understood, the x-ray analysis of the ground powders and the metallographic evaluation of the consolidated materials give often quite different results. Experiments are now underway to determine the Mo solid solution content of the powders by x-ray diffraction of metallographically mounted and ground powders. It is hoped that this approach will provide more accurate Mo solid solution volume fractions of the powders.

Ingots with the compositions Mo-3Zr-12Si-8.5B and Mo-5Zr-12Si-8.5B (at. %) were prepared by arc-melting and subsequently annealed for 24 hours at 1600C. The first alloy had a slightly lower room temperature fracture toughness than an earlier alloy containing 1.5 at. % Zr. The second alloy with 5 at. % Zr was too brittle to be tested. In order to determine the optimum Zr concentration, an alloy containing 1 at. % Zr will soon be examined.

A symposium with the title "Beyond Nickel-Base Superalloys" has been proposed for the TMS 2004 Annual Meeting in Charlotte, NC. The symposium has been approved and has attracted a total of 59 abstracts covering primarily molybdenum silicides, niobium silicides, and precious metal superalloys.

## ISSUES

None

| **Report Prepared By** | **Date** |
|---|---|
| Joachim H. Schneibel | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| UT-2(A) | Study of Fatigue and Fracture Behavior of Cr-Based Alloys and Intermetallic Materials | 11X-SP173V | 09/15/93 | 03/15/04 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| The University of Tennessee<br>Department of Materials Science and Engineering<br>Knoxville, TN 37996-2200 | P. K. Liaw |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 1 |
| Total Current Year Commitment $K] | 78 |
| Projected Current Year Costs [$K] | 78 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 68 | 70 | 72 | 49 | 51 | 53 | 55 | 57 | 59 | 61 | 64 | 66 |
| Actual Costs | | | | 47 | 49 | 51 | 53 | 55 | 58 | 61 | 64 | 69 |
| Variance | 68 | 70 | 72 | 2 | 2 | 2 | 2 | 2 | 1 | 0 | 0 | (3) |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| UT-2(A)-1 | Study the finite element modeling of fracture behavior of Cr-Ta alloys. | 02/28/02 | | 02/28/02 |
| UT-2(A)-2 | Investigate the eutectic composition of Cr-Ta alloys. | 03/31/02 | | 03/31/02 |
| UT-2(A)-3 | Develop methods to monitor the chemical compositions during processing. | 07/15/02 | | 07/15/02 |
| UT-2(A)-4 | Heat treat Cr-Ta alloys. | 10/31/03 | | 10/31/02 |
| UT-2(A)-5 | Directionally solidify Cr-Ta and Cr-Ta-Mo alloys. | 02/28/03 | | 02/28/03 |
| UT-2(A)-6 | Determine and compare the eutectic points of Cr-Ta and Cr-Ta-Mo alloys. | 05/31/03 | | 05/31/03 |
| UT-2(A)-7 | Develop the lamellar structures of Cr-Ta and Cr-Ta-Mo alloys. | 12/31/03 | | |
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## TECHNICAL HIGHLIGHTS

The objectives of the present project are (1) to investigate the formation of a well-aligned lamellar structure in the Cr-based alloys reinforced by the Cr2Ta Laves phase, (2) to elucidate the feasibility of employing the Cr-based alloy with a lamellar structure in the ultra-high temperature applications, and (3) to develop a possible low-cost process for industry-scale production of this advanced alloy.

A high-temperature optical floating-zone furnace has been used to directionally-solidify (DS) Cr-Ta alloys and to provide lamellar structures. In the furnace, light beams from the Xenon lamp were reflected by the mirrors and then focused on the bar sample to form a molten zone, and the mechanical system provided a downward movement of the sample and the seed bar to move the remelted zone along the length direction of the specimen. Thus, a directionally-solidified microstructure was obtained. In addition, a rotation movement was incorporated to improve the microstructural homogeneity during directional solidification.

A fine lamellar structure in the drop-cast eutectic Cr-Ta sample was observed. However, the microstructures in the DS sample had a cellular feature, indicating the instability of the liquid/solid interface during the growth process.

## ISSUES

| Report Prepared By | Date |
|---|---|
| P. K. Liaw | 10/22/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| ORNL-3H | Low-Cost Manufacturing of Membranes | FEAA028 | | |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>P. O. Box 2008<br>Oak Ridge, TN 37831-6063 | T. Armstrong<br>B. Armstrong<br>C. Blue |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | |
| Total Current Year Commitment $K] | 150 |
| Projected Current Year Costs [$K] | |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 17 | 33 | 50 | 66 | 83 | 100 | 116 | 133 | 149 | 165 | 182 | 200 |
| Actual Costs | 30 | 36 | 38 | | | | | | | | | |
| Variance | (13) | (3) | 12 | 66 | 83 | 100 | 116 | 133 | 149 | 165 | 182 | 200 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| 1 | Develop tungsten sintering apparatus and test | 06/30/03 | 04/15/03 | 04/15/03 |
| 2 | Scale up sample size with new device | 12/30/03 | | |
| 3 | Demonstrate deposition of ceramic membranes on metallic supports | 09/30/03 | | |
| 4 | Demonstrate proof-of-concept for sintered membrane on metallic support | 09/30/04 | | |
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## TECHNICAL HIGHLIGHTS

This quarter work was initiated to use a tungsten halogen lamp for sintering YSZ deposited on Ni-YSZ supports. The results of the tests carried out to determine the feasibility of this concept indicated that the lamp could not attain a high enough temperature to sintering the thin zirconia films on the porous supports. Therefore, further experimentation was terminated.

Tests were also initiated on deposition of thin ion (proton) transport membranes on porous metallic supports. ORNL has obtained porous metallic supports from Pall Corporation with an average pore size of 2 microns. ORNL is depositing coating of novel proton conductors under development in ano0ther FE project by both wet and dry processes. Initial test are being carried out on Lanthanum zirconate, La2Zr2O7. Materials are being synthesized using combustion synthesis, coarsening by heat treatment, and prepared into colloids by polymeric stabilization in water.

It is anticipated that membranes will be prepared during the next quarter.

## ISSUES

None

| Report Prepared By | Date |
|---|---|
| T. Armstrong | 01/20/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| 01 | Solid State Electrolyte Systems | 12461 | 10/01/02 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Pacific Northwest National Laboratory<br>902 Battelle Blvd<br>P.O. Box 999<br>Richland WA 99352 | K Scott Weil |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 15 |
| Total Current Year Commitment $K] | 465 |
| Projected Current Year Costs [$K] | 410 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 35 | 70 | 104 | 138 | 172 | 206 | 240 | 274 | 308 | 342 | 376 | 410 |
| Actual Costs | 4 | 23 | 29 | 30 | 40 | 61 | 106 | 129 | 163 | 183 | 220 | 275 |
| Variance | 31 | 47 | 75 | 108 | 132 | 145 | 134 | 145 | 145 | 159 | 156 | 135 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| 3-1 | Assess the viability of the braze with Al2O3 | 11/30/02 | | 11/30/02 |
| 3-2 | Optimize the braze for use in oxygen separation applications | 02/28/03 | 05/30/03 | 05/30/03 |
| 3-3 | Assess the viability of the braze with cerate | 05/31/03 | 07/31/03 | |
| 3-4 | Conduct age testing of membrane/braze/support structure joints for both O2 and H2 separation applications | 09/30/03 | 11/30/03 | 09/30/03 |
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## TECHNICAL HIGHLIGHTS

Development and Exposure Testing of Aluminum-Based Air Brazes
(Partial Completion of Milestone 3-4 for FY2003)
We have previously reported our work on the new ceramic joining process we have developed on this program, reactive air brazing (RAB). To date, the research has focused on the silver-copper oxide system as the basis for the reactive air braze. We are now examining the effects of alloying additions on the base properties of the braze, including its liquidus temperature and wettability on various substrates, as well as on the subsequent properties of the resulting joints, including maximum use temperature, strength, and high-temperature oxidation resistance. Initial alloying experiments were conducted with aluminum in an effort to determine whether the melt and re-melt temperatures of the braze could be substantially separated to effect a lower temperature joining process. Surprisingly, we found that alumina could be brazed in open air using pure aluminum foil. It was determined that although the joint is not as strong as the base ceramic substrate, it is quite ductile and will plastically deform under high stress. What is particularly surprising though, is that the aluminum air brazed joints retain their ductility and increase measurably in strength after extended exposure to high temperature oxidation conditions. Based on these results, we feel that aluminum can form the basis of a new family of air brazes for ceramic joining and that the final properties of the resulting joints should be tailorable via appropriate alloying modifications to the aluminum. In particular, greater joint strengths should be obtainable by mitigating interfacial porosity in the joint. The microstructural changes and corresponding effects on joint strength associated with more extensive aluminum to alumina conversion within the braze filler will be also studied in the future.

Exposure Testing of Ag-CuO Brazes for Potential Air Separation Membranes
(Partial Completion of new Milestone 3-4 for FY2003)
Four point bend strength testing was conducted on (La0.6Sr0.4)(Co0.2Fe0.8)O3 (LSCoF) samples brazed together with the Ag-CuO air braze. Braze compositions varied from a silver to copper oxide ratio of 20:80 to 99:1. The specimens were tested in the as-brazed and as-aged conditions. Aging was conducted in air at 750°C for upwards of 1000hrs. Specimens were removed at 200hr intervals, bend strength tested, and examined using SEM and EDX. Initial results demonstrate that the flexural strength in the as-brazed specimens is optimized at a braze composition of 4 mol% CuO in Ag. Long-term aging appears to have no significant effect on the bend strength of specimens brazed with this composition. Testing is continuing on the aged "off-optimal" compositions to determine whether the optimal braze composition shifts as a function of exposure time (e.g. whether X mol % CuO in Ag, where X does not equal 4, offers greater flexural strength when the joints are aged at temperature).

Papers Submitted Publication During the 4th Quarter of FY2003

1. K. S. Weil, J. Y. Kim, and J. S. Hardy, "Reactive Air Brazing: A New Method of Sealing Solid Oxide Fuel Cells and Other High Temperature Devices," Journal of Materials Research, in review.

2. J. Y. Kim, J. S. Hardy, and K. S. Weil, "Effects of CuO Content on the Wetting Behavior and Mechanical Properties of a Ag-CuO Braze for Ceramic Joining," Journal of the American Ceramic Society, in review.

3. K. S. Weil, J. S. Hardy, and J. Y. Kim, "A New Technique for Joining Ceramic and Metal Components in High Temperature Electrochemical Devices," invited paper, Journal of Advanced Materials, in review.

4. J. S. Hardy, J. Y. Kim, and K. S. Weil, "Joining Mixed Conducting Oxides Using an Air-Fired Electrically Conductive Braze," Journal of the Electrochemical Society, in review.

5. J. Y. Kim, J. S. Hardy, and K. S. Weil, "Use of Aluminum in Air Brazing Aluminum Oxide," Journal of Materials Research, in review.

## ISSUES

Note regarding Milestone 3-3: Alternative oxide materials are being considered in the FE-ARM program for solid state hydrogen separation. Braze assessment with these materials will be conducted once the leading candidates are identified.

| Report Prepared By | Date |
|---|---|
| K Scott Weil | 10/10/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| LANL-3 | Efficient Production of Hydrogen using Pd Membrane Reactors | | 10/01/98 | 09/30/05 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Los Alamos National Laboratory<br>P.O. Box 1663, MS-C348<br>Los Alamos, NM 87545 | Stephen A. Birdsell |

## BUDGET AND COST REPORT

| | |
|---|---|
| Prior Year Funds [$K] | 153 |
| Total Current Year Commitment $K] | 253 |
| Projected Current Year Costs [$K] | 253 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned Costs | 10 | 10 | 10 | 15 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| Actual Costs | 1 | 1 | 4 | 9 | 3 | 5 | 18 | 8 | 9 | 11 | 20 | 24 |
| Variance | 9 | 9 | 6 | 7 | 22 | 20 | 7 | 17 | 16 | 14 | 5 | 1 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| LANL-3-1 | Continue to develop and test Pd membranes | 09/30/03 | | 09/30/03 |
| LANL-3-2 | Continue PMR development and testing using the most promising membranes | 09/30/03 | | 09/30/03 |
| LANL-3-3 | Present paper describing progress of Pd Membrane and advanced PMR development at the Fossil Energy Conference | 04/24/03 | | 04/24/03 |
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## TECHNICAL HIGHLIGHTS

Initial testing of a Pd/V-Cu/Pd composite membrane was accomplished. The hydrogen flux through the 40 micron thick V-Cu alloy foil coated with 100 nm of Pd on each side was 0.32 mol (STP)/m2s (42.62 sccm/cm2min) at 350C and a pressure differential across the membrane of 4.5 atm. Testing of this type of membrane will continue.

## ISSUES

| Report Prepared By | Date |
|---|---|
| Stephen A. Birdsell | 10/17/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| IMTL-3 | Development of Ceramic Membranes for Hydrogen Separation | FEAA028 | 10/01/87 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| Oak Ridge National Laboratory<br>One Bethel Valley Road<br>P. O. Box 2008<br>OAK RIDGE, TN 37831 | R. R. Judkins |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 13 |
| **Total Current Year Commitment $K]** | 338 |
| **Projected Current Year Costs [$K]** | 351 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 29 | 58 | 88 | 117 | 146 | 175 | 205 | 234 | 263 | 293 | 322 | 351 |
| **Actual Costs** | 12 | 15 | 28 | 65 | 91 | 143 | 242 | 320 | 321 | 347 | 348 | 350 |
| **Variance** | 17 | 43 | 60 | 52 | 55 | 32 | (37) | (86) | (58) | (54) | (26) | 1 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| IMTL-3-1 | Demonstrate an improved hydrogen separating membrane using He as a surrogate for hydrogen. | 03/31/03 | | 02/28/03 |
| IMTL-3-2 | Completed development of optimum support material for membrane. | 06/30/03 | | 09/30/03 |
| IMTL-3-3 | Submit prototype hydrogen separation membrane sample for non-proliferation review (NPR) and classification approval. | 09/30/03 | 10/31/03 | |
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## TECHNICAL HIGHLIGHTS

The membranes test systems have been modified so that hydrogen and propane can be used for test gases in addition to the helium and sulfur hexafluoride. The ideal separation factor and measured separation factor for hydrogen from propane can be determined up to approximately 500 Celsius. Testing of one of the metal supported membranes has just begun with hydrogen and propane.

## ISSUES

None.

| Report Prepared By | Date |
|---|---|
| B. S. Miller for R. R. Judkins | 10/15/03 |

# Quarterly Management Report

| WBS Element | Project Title | Contract Number | Contract Start | Contract End |
|---|---|---|---|---|
| | Metallic Filters for Hot gas Cleanup | W-7405-Eng-82 | 10/01/99 | 09/30/03 |

| Performer Name and Address | Principal Investigator(s) |
|---|---|
| I.E. Anderson<br>222 Metals Development<br>Ames Laboratory, Iowa State University<br>Ames, IA 50011 | I.E. Anderson 515-294-9791<br>B. Gleeson 515-294-4446 |

## BUDGET AND COST REPORT

| | |
|---|---|
| **Prior Year Funds [$K]** | 35 |
| **Total Current Year Commitment $K]** | 90 |
| **Projected Current Year Costs [$K]** | 100 |

| | O | N | D | J | F | M | A | M | J | J | A | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Planned Costs** | 8 | 16 | 24 | 32 | 40 | 49 | 58 | 67 | 76 | 84 | 92 | 100 |
| **Actual Costs** | 3 | 6 | 10 | 17 | 23 | 26 | 32 | 40 | 45 | 72 | 75 | 85 |
| **Variance** | 5 | 10 | 14 | 15 | 17 | 23 | 26 | 27 | 31 | 12 | 17 | 15 |

## MILESTONE REPORT

| Milestone Designation | Milestone Description | Due Date | Revised Due Date | Completion Date |
|---|---|---|---|---|
| FY03-1 | Analyze filter element samples of selected alloys from the field test(s) in a coal-fired PFBC | 09/30/03 | | 09/30/03 |
| FY03-2 | Establish alloy with best field test performance and report on filter characteristics | 09/30/03 | | 09/30/03 |
| FY-03-3 | Fabricate field test filter section for active filtration testing | 09/30/03 | | 09/30/03 |
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## TECHNICAL HIGHLIGHTS

This past quarter primarily involved testing of our Ni-Cr-Al-Fe filters alloys in the combustion conditions generated by a slagging furnace system (SFS) at the University of North Dakota Energy and Environmental Research Center (EERC). This system is capable of achieving furnace exit temperatures of 1483 - 1593° C to ensure that the ash in the main combustor is molten and flowing. Within this system there are 2 locations/temperatures at which sample coupons can be subjected to the gas environment of the SFS combustor. The high temperature (slagging) location is approximately 980° C, while a cooler temperature zone is located down stream in a heat exchanger elbow which is typically at approximately 700° C. For the oxygen blown coal-fired test conditions, 4 porous (approx. 70% dense) sintered o-rings having a 60 mm OD x 25 mm long x 0.5 mm thick wall of the Ni-Cr-2xAl-Fe filter alloy were inserted in both the convective pass (2 o-rings) and heat exchanger test zones (2 o-rings) of the SFS chamber. SFS combustor gas environment test conditions were established by exposure for 100 h under natural gas-firing conditions followed by 8.75 h of coal firing. Under this test condition the test coupons were exposed to a gas environment containing 1840 ppm SO2 at temperatures of 921°C at the convective pass and 604°C at the heat exchanger. It was found that the filter samples underwent minimal degradation, where < 2um of surface attack was noted after exposure at 921°C and essentially no surface attack was detected microstructurally after exposure at 604°C. These preliminary results substantiate the laboratory-scale tests, by showing the exceptional resistance to high-temperature degradation of the Ni-Cr-Al-Fe filters alloys developed in this study.

Further porous filter sheet processing developments involved a minor alloy redesign effort that was motivated by the findings of the previous quarter, which involved detailed characterization of filter sample cross-sections. These findings indicated that prolonged sintering time promoted coarsening of an Al-rich Ni3Al (beta) phase in the sintered neck regions of samples made from Ar-atomized Ni-Cr-2xAl-Fe powder. The beta phase coarsening resulted in local Al-depleted regions at the surfaces which could have increased oxidation properties, as well as, could have an embrittling effect on the porous structure. Thus, we performed a small matrix of alloy design experiments, guided by the Ni-Cr-Al ternary phase diagram, to develop a composition that contained sufficient Al concentration, but did not generate the beta phase after annealing at the sintering temperature of 1250°C. The test alloys (in wt.%) included Ni-16Cr-9Al-3Fe (termed Ni-Cr-2xAl-Fe), Ni-16Cr-9Al, Ni-16Cr-7.87Al, and Ni-16Cr-6.75Al, which were chill cast. Microstructural examination of the specimens that were furnace cooled (10°/min) after annealing for 1 hr. revealed that both of the richest Al alloys contained partially decomposed beta phase, while the Ni-16Cr-7.87Al and Ni-16Cr-6.75Al alloys had only a gamma/gamma prime precipated microstructure, as desired. Thus, the preferred powder composition for future work in the model system should contain some slight Al-enrichment of the Ni-16Cr-7.87Al composition, less than 9Al, to avoid beta phase, but to have the maximum available Al content for uniform oxide scale formation after sintering of the porous structure. Additional porous o-ring samples (rolled and welded) of the Ni-Cr-2xAl-Fe and Ni-Cr-Al-Fe alloy powders (2 of each alloy) were fabricated for additional testing in the coal-fired SFS unit at at EERC, under the supervision of John Hurley, where sample analysis should be possible by the end of the next quarter. A presentation and paper on this work will be delivered at the TMS Fall meeting in Chicago in November.

## ISSUES

Due to a request from the technical program manager for this ARM project, a redirected project will begin in FY2004 entitled, "Improved Atomization Processing For Fossil Energy Applications." While the work of this current report involves gas atomization, but includes metal powder sintering and corrosion testing of alloys suited for hot gas filtration applications, the new project will focus only on improvement of the gas atomization process for a variety of purposes. Note that a brief transition period is needed to complete the on-going tasks related specifically to the filtration studies and the new milestones for the first quarter of FY2004 will reflect this fact.

| Report Prepared By | Date |
|---|---|
| I.E. Anderson | 10/17/03 |